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Title: FY2014 CERAMIC FUELS DEVELOPMENT ANNUAL HIGHLIGHTS

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# ***FY2014 CERAMIC FUELS DEVELOPMENT ANNUAL HIGHLIGHTS***

LA-UR-14-27363

***Prepared for  
U.S. Department of Energy  
FCRD Program***

***Compiled by  
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Los Alamos National Laboratory***

## SUMMARY

Key challenges for the Advanced Fuels Campaign (AFC) are the development of fuel technologies to enable major increases in fuel performance (safety, reliability, power and burnup) beyond current technologies, and development of characterization methods and predictive fuel performance models to enable more efficient development and licensing of advanced fuels. Recent AFC changes have targeted transmutation fuel development on metal fuel only and shifted the ceramic fuel development focus solely to Advanced Light Water Reactor (LWR) Fuels. Ceramic fuel development activities for fiscal year 2014 (FY14) fell within the areas of 1) National and International Technical Integration, 2) Advanced Accident Tolerant Ceramic Fuel Development, 3) Advanced Techniques and Reference Materials Development, and 4) Fabrication of Enriched Ceramic Fuels. High uranium density fuels were the focus of the ceramic fuels efforts. Accomplishments for FY14 primarily reflect the prioritization on identification and assessment of new ceramic fuels for LWRs which would have enhanced accident tolerance while also maintaining or improving normal operation performance, and exploration of advanced post irradiation examination techniques which will support more efficient testing and qualification of new fuel systems. Significant accomplishment include:

- In a close collaboration between LANL and JAEA researchers, the influence of defects associated with non-stoichiometry on thermophysical properties is being evaluated in detail for  $(\text{U,Ce})\text{O}_2$  and being extended to MOX fuel studies. This data will help improve understanding of fuel behavior under irradiation. These experiments also provide insight and guidance for development of advanced fuel systems that can have improved performance under accident conditions.
- In a collaboration between LANL, ORNL and BNL, initial screening and assessment of new, advanced ceramic fuels was performed with a specific goal of achieving enhanced accident tolerance while maintaining economic and performance characteristics necessary for near-term deployment in existing LWR reactors. By coupling thermodynamic analysis with material compatibility screening experiments and assembly level neutronic analysis, several candidate composite systems were shown to merit further study and are being examined in more detail for ATF-1 irradiation testing. Thermo-physical properties of the pure high fissile density silicide phases and several UN- $\text{U}_3\text{Si}_5$  composites were determined for the first time on unirradiated materials. It should be noted that this activity compliments the industry-lead FOA projects on accident tolerant fuel development.
- Irradiation test design and fabrication process development were initiated on UN-15vol% $\text{U}_3\text{Si}_5$  composite fuel as part of the ATF-1 irradiation test series. The preliminary test design was performed for the first time using BISON to quickly narrow down on the rodlet-capsule and fuel/rodlet gaps. The test will also include monolithic  $\text{U}_3\text{Si}_5$  rodlets as basic irradiation performance data such as swelling behavior is not available for this phase of the composite fuel. A commercial FeCrAl alloy (Kanthal AF) was selected as the cladding to allow data to be gathered for this material as well during the fuel irradiation test.
- Rapid, low temperature field assisted sintering was improved for  $\text{UO}_2$  achieving a density of over 93% theoretical density within two minutes at 600°C. Extension of these same rough FLASH sintering parameters was surveyed for high uranium density silicide, nitride and boride phases and composites. Not unexpectedly, it was found that field assisted sintering parameters will need to be tailored to each material system with several systems requiring



higher currents for rapid densification. This work supports an INERI with EURATOM which began in FY14 and continues through FY16.

- Development of advanced, non-destructive pre- and post-irradiation examination (PIE) techniques continued with demonstration of the benefits of coupling neutron imaging with diffraction data in order to characterize microstructure and chemistry in 3-D. More efficient data analysis processes are being developed to allow quantification of spatial and chemical resolution.

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**ACRONYMS**

AFC	Advanced Fuels Campaign
ASU	Arizona State University
ATF	Accident Tolerant Fuel
ATR	Advanced Test Reactor
BNL	Brookhaven National Laboratory
CEA	Commissariat à l'énergie atomique et aux énergies alternatives
CIAE	China Institute of Atomic Energy
CNWG	Civil Nuclear Energy Working Group
CRIEPI	Central Research Institute of Electric Power Industry
CTR-N	Carbothermic Reduction-Nitridization
DOE	Department of Energy
DOT	Department of Transportation
ECCS	Emergency Core Cooling System
EOC	End of equilibrium Cycle
EURATOM	European Atomic Energy Community
FAST	Field Assisted Sintering Technique
FCCI	Fuel Clad Chemical Interaction
FCRD	Fuel Cycle R&D
FOA	Funding Opportunity Announcement
FS	Flash Sintering
FY	Fiscal Year
IFBA	Integral Fuel Burnable Absorber
INERI	International Nuclear Energy Research Initiative
INL	Idaho National Laboratory
IRP	Industry Research Proposal
ITU	Institute for Transuranium Elements
JAEA	Japan Atomic Energy Agency
KAERI	Korea Atomic Energy Research Institute
LANL	Los Alamos National Laboratory
LANSCE	Los Alamos Neutron Science Center
LB-LOCA	Large Break – Loss-Of-Coolant Accident
LHGR	Linear Heat Generation Rate

LLNL	Lawrence Livermore National Laboratory
LVDT	Linear Variable Displacement Transducer
LWR	Light Water Reactor
MA-MOX	Minor Actinide – Mixed Oxide Fuel
MOX	Mixed Oxide Fuel
MARIE	Matter-Radiation Interactions in Extremes
NDE	Non-Destructive Examination
NEA	Nuclear Energy Agency
NEUP	Nuclear Energy University Proposal
OECD	Organization for Economic Co-operation and Development
OIM	Orientation Imaging Microscopy
ORNL	Oak Ridge National Laboratory
PCT	Peak Cladding Temperature
PICT	Peak Internal Cladding Temperature
PWR	Pressurized Water Reactor
PIE	Post Irradiation Examination
QMS	Quadrupole Mass Spectrometer
R&D	Research and Development
Rosatom	Rosatom State Atomic Energy Corporation
SEM	Scanning Electron Microscopy
SET	Separate Effects Testing
SFR-AF	Sodium Fast Reactor – Advanced Fuels Arrangement
SPS	Spark Plasma Sintering
TAF-ID	Thermodynamics of Advanced Fuels-International Database
TD	Theoretical Density
TGA	Thermogravimetric Analysis
TPOC	Technical Point of Contact
USC	University of South Carolina
WEC	Westinghouse Electric Company
XRD	X-Ray Diffraction

## 1. Introduction

Ceramic fuel development for FY14 focused on composite fuel and was a balance of effort seeking transformational R&D while also incrementally advancing fuel technology. The fundamental, science-based approach employed in this area relies upon close coordination of theoretical, experimental and modeling efforts.

In light of the Fukushima Daiichi nuclear disaster, continued emphasis was placed upon increasing the ability to understand and improve the accident behavior of light water reactor (LWR) fuel. A range of material systems can offer enhanced oxidation resistance or fission product retention, but the challenge in deploying new fuel designs in commercial reactors rests in the need to utilize the existing fuel fabrication infrastructure, meet existing licensing requirements, and retain fuel cycle and plant economy. Research is being conducted within the ceramic fuels technologies area for efficient development of accident tolerant fuels i) taking an evolutionary path based upon  $\text{UO}_2$  fuels, ii) taking a revolutionary path based upon composite fuels, and iii) developing advanced fabrication and characterization technologies that can enable and accelerate development of the fuels with enhanced accident tolerance.

Exploratory work has been undertaken to study the performance benefits that may be realized through minor modifications to reference uranium dioxide that would be largely transparent to fuel fabricators, operators, and licensing requirements (evolutionary path). Three criteria were developed by which reactor fuel itself could be improved that would offer advantages to both normal steady state operation as well as transients and long term storage. First, improved fracture toughness and plasticity could relieve fuel pellet cracking and missing surfaces that not only introduce uncertainties during reactor startup and operation, but also provide free surfaces that accelerate fission product and transuranic release during a full breach. Second, enhanced thermal conductivity would provide clear benefits to normal operation as well as some advantages to loss of coolant accidents and reactivity insertions under certain conditions. Finally, enhanced oxidation resistance would increase coping time before fuel pulverization occurs and would also enhance stability during wet or dry storage of used fuel.

A second approach to development of fuels with enhanced accident tolerance is exploration of advanced composite systems (revolutionary path) with the potential to improve the accident performance of light water reactor fuels as well as offer benefits to normal operation. Composite fuels have been of interest for many decades, as a wide range of both ceramic and metallic alloys can be envisioned that would surpass the performance of traditional LWR oxide ceramic fuels. However, when systems are explored within the constraint of use in existing commercial LWRs, the practical limit on uranium-235 enrichment creates significant challenges in the introduction of non-fissile second phases. Any inert second phase incorporated in a proposed fuel must be limited to extremely low volume fractions if reactor performance is not sacrificed and enrichment remains fixed. It is difficult for such concepts to achieve improvement in any of the critical metrics (e.g. thermal conductivity, mechanical properties, or thermochemical stability) when limited in such a way. One option that may overcome this constraint is the use of uranium bearing second phases. Although they may not contain the uranium density of uranium dioxide or uranium nitride, a phase containing even half the uranium density of these reference ceramics may provide sufficient margin to retain reactor operation within a fixed enrichment. A wide range of uranium compounds have been investigated historically, many of which could be envisioned to offer intriguing benefits to accident performance as well as the overall fuel attributes. Also, changes of cladding and core materials to improve accident behavior can have a negative neutronic impact relative to current operations, but high uranium density fuels may compensate

for some neutronic penalties and thus help enable change to core materials with enhanced accident tolerance.

Another critical area for more rapid and efficient development of ceramic fuels is development of advanced techniques for fuel fabrication and for characterization of irradiated fuels. Advanced sintering techniques can not only enable cost savings and product quality improvement for fuel manufacture but to composite fuel systems, these techniques may enable fuel systems that can not be fabricated by conventional means. Also, the ability to effectively evaluate irradiated fuel pins/rodlets for composition, defects such as cracking, voids and second phases, as well as cladding interactions prior to conducting destructive PIE is critical to informing modeling and simulation and provide more rapid and greater feedback on the effects of irradiation on the fuel and cladding. Another benefit of improving and using advanced NDE characterization techniques is that regions of interest in the irradiated fuel rod can be precisely probed and help reduce costly and time consuming destructive characterization work while generating large data sets. For example, if an unexpected or unidentifiable artifact is identified at a specific location in the test rodlet, destructive PIE can then be used to fully characterize only that region opposed to the expensive and time consuming serial sectioning that must be done in the absence of NDE characterization. This capability can then in turn allow for accelerated acceptance of new fuel forms and advance the fuel licensing process leading to more efficient fuels and safer reactors.

As noted earlier, key challenges for the Advanced Fuels Campaign (AFC) are the development of fuel technologies to enable major increases in fuel performance (safety, reliability, power and burnup) beyond current technologies, and development of characterization methods and predictive fuel performance models to enable more efficient development and licensing of advanced fuels. In support of addressing those key challenges, the ceramic fuel technologies development activities fell within areas of 1) National and International Technical Integration, 2) Advanced Accident Tolerant Ceramic Fuel Development, 3) Advanced Techniques and Reference Materials Development, and 4) Fabrication of Enriched Ceramic Fuels. Highlights from the FY14 ceramic fuel development R&D are provided in this document.

## **2. National and International Technical Integration**

AFC researchers are very active in international collaborations with Korea, France, Japan, China, Russia, and EURATOM. These interactions and collaborations are managed through a combination of participation in Generation IV Global International Forum projects, International Nuclear Energy Research Initiative (INERI) projects, and participation in bilateral and trilateral government-to-government agreements. The ceramic fuels areas have collaborations primarily under the headings of Advanced Fuels within the US/Japan bilateral and the GenIV SFR. There are also collaborations on Field Assisted Sintering and Thermodynamics of Nuclear Fuels under US/EURATOM arrangements.

### **2.1 GenIV-Sodium Fast Reactor Arrangement on Advanced Fuels**

*K.J. McClellan, [kmcclellan@lanl.gov](mailto:kmcclellan@lanl.gov), LANL*

The Sodium Fast Reactor Advanced Fuel (SFR-AF) arrangement started in 2007 with a targeted duration of 10 years within the frame of the Generation IV Sodium Fast Reactor program. The primary objective is to investigate high burn-up Minor Actinide bearing fuels as well as cladding and wrapper materials capable of withstanding high neutron doses and temperatures. The project has been structured in 3 steps: evaluation of advanced fuels and materials options, Minor-Actinide bearing fuels evaluation, and assessment of high burn-up capability of advanced fuel(s) and materials. Until this point, participants in the arrangement have been the DOE, CEA, JAEA, KAERI, and EURATOM. China and Russia have petitioned to join the arrangement with contributions from CIAE and Rosatom, respectively. In 2014, the US is serving as co-chair for the AFR-AF program management board and hosted the spring meeting in Knoxville, TN. The proposed contributions of China and Russia were discussed with the relevant negotiators, subsequently approved by the board and the AFR-AF arrangement was modified to incorporate those contributions. The modified arrangement was subsequently approved by the SFR-System Steering Committee and has been transmitted to the signatories of the participating countries for final approval.

### **2.2 US/Japan CNWG Collaboration on Advanced Fuels**

*K.J. McClellan, [kmcclellan@lanl.gov](mailto:kmcclellan@lanl.gov), LANL*

Cooperative research under the Advanced Fuels area of the Fuel Cycle R&D and Waste Management Sub-Working Group is performed under the general areas of properties, performance and analysis. The goal of this effort is to perform collaborative R&D for evaluation of basic properties and irradiation behavior of advanced fuels. The objectives of the collaboration are to expand the basic properties and performance data and to improve understanding of advanced fuels with an emphasis on employment of advanced experimental techniques. Through incorporation of new MA-MOX irradiation data the effort will also enable development and application of advanced modeling and simulation tools for design and performance analysis of oxide fuels. In FY14, several technical expert meetings were held in Japan and in the US at LANL and INL to advance specific tasks on basic properties of fuels, development of PIE data, and modeling and simulation of irradiated transmutation MOX fuel. Several joint publications from the fuel properties activities were made during the period and initial planning started for future power-to-melt and steady states tests of MA-MOX on the Joyo reactor.

A key aspect of the collaboration is a visiting JAEA scientist working at LANL on basic fuel properties. A highlight of the research by the current visiting scientist (JAEA has committed to funding one visiting scientist per year) follows.

## 2.2.1 Oxygen Thermochemistry of Urania-Rare Earth System: $\text{UO}_2\text{-CeO}_2$

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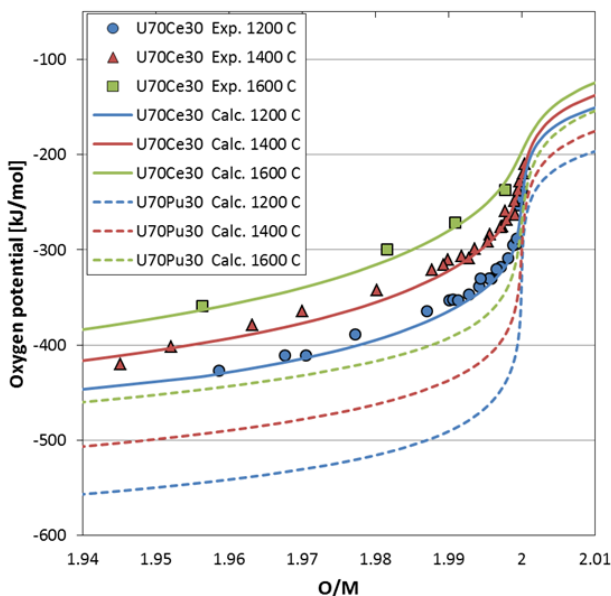
Collaboration between the DOE and Japan on characterization of the properties of nuclear materials under the Civil Nuclear Energy Research and Development Working Group (CNWG) remains an area of active progress. CNWG targets to co-develop nuclear fuel technology by leveraging facilities and resources belonging to both Japan and the US. Although the Japan Atomic Energy Agency (JAEA) research focuses on  $(\text{U,Pu})\text{O}_2$  as mixed oxide (MOX) fuel and the DOE program's focus currently is on metallic transmutation fuel, the effects of Ce on the thermochemistry and thermophysical properties of oxide fuel represent a common interest to both programs given the utility of Ce as a surrogate for Pu as well as its importance as a fission product. Many studies have been reported on  $(\text{U,Ce})\text{O}_2$  as  $\text{UO}_2$  with a fission product and a surrogate material of  $(\text{U,Pu})\text{O}_2$  since Ce is one of most prevalent fission products forming full solid solution over  $1000^\circ\text{C}$ . Furthermore, its  $3+/4+$  valence mirrors that of Pu, making it a suitable thermochemical surrogate.

Thermal conductivity is one of the most critical thermophysical properties for nuclear fuel operation. It is well understood that both cation defects and oxygen defects will significantly affect thermal

conductivity. Both are present in MOX fuel, but characterization of their respective roles is challenging given the requirements of Pu operations. Thermal conductivity of  $(\text{U,Ce})\text{O}_2$  has been systematically studied as a function of Ce content, however, reports on the oxygen non-stoichiometry of  $(\text{U,Ce})\text{O}_2$  are limited. It is necessary to have a firm understanding of the relationship between oxygen activity and the oxygen-to-metal ratio (O/M) in order to precisely control the latter to facilitate thermophysical property measurement as a function of specific defect structures.

Experimental measurements of the oxygen potential were conducted on 20% and 30% Ce compositions using the gas equilibrium method where oxygen partial pressure in the atmosphere was controlled with mixing dry/wet  $\text{Ar}/\text{H}_2$  gas. The composition simulates Pu content in advanced MOX fuel in JAEA. More than 100 data points were obtained in the O/M range of 1.945 ~ 2.000 at  $1200^\circ\text{C}$ ,  $1400^\circ\text{C}$  and  $1600^\circ\text{C}$ . Ongoing work is focused on executing identical measurements on more dilute Ce contents that better represent levels expected of Ce as a fission product.

The experimental result of  $(\text{U}_{0.7}\text{Ce}_{0.3})\text{O}_2$  is shown in Fig 1 together with calculated result by defect chemistry and  $(\text{U}_{0.7}\text{Pu}_{0.3})\text{O}_2$  data. The experimental results are well reproduced by the defect analysis and the error was observed to be  $8.7\text{kJ/mol}$  ( $n=57$ ). From the comparison with that



**Figure 1: Oxygen potential – O/M ratio developed for  $\text{U}_{70}\text{Ce}_{30}$  and  $\text{U}_{70}\text{Pu}_{30}$  analyzed by defect chemistry based on the experimental results by gas equilibrium method.**

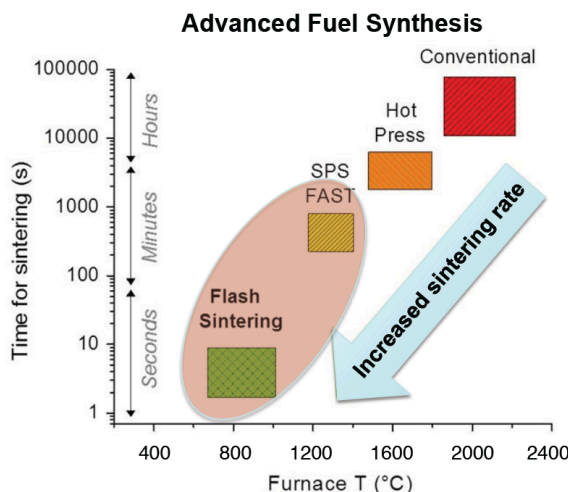


of  $(U_{0.7}Pu_{0.3})O_2$ , applicability of the same defect chemistry and S-style curve shown in the Fig 1 are common.  $(U,Ce)O_2$  requires a higher oxygen potential for an equivalent O/M ratio compared to  $(U,Pu)O_2$ . This oxygen potential data has enabled ongoing property studies, and is important information in evaluating the analogies as a surrogate of  $(U,Pu)O_2$ .

## 2.3 US/EURATOM I-NERI Project on Novel Technology for Synthesis of Nuclear Fuels

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This three-year project was initiated in FY14 to investigate advanced net shaping technology for nuclear fuel/target applications. The U.S. contribution to this collaborative research effort is performed under the FCRD advanced fuels campaign while the EURATOM contribution is performed under the EURATOM FP7 and HORIZON 2020 programs on Safety of Nuclear Fuel.



**Figure 2: Influence of electric field to reduce sintering times and temperatures for ceramic fuels.**

The objective is to advance the field of novel compaction technology for advanced fuel systems where conventional routes are not viable. Advanced fuels being studied for enhanced accident tolerance and for actinide transmutation often have unique characteristics which make conventional sintering routes undesirable for or incapable of yielding the required fuel pellet characteristics and this project explores processing routes to enable more efficient fuel synthesis via reducing processing time and/or temperature (Fig. 2).

This project integrates the various embryonic advanced processing activities ongoing at each participating institution which will in turn allow this effort to encompass several field assisted sintering techniques employed for a range of ceramic systems. The

primary techniques and materials systems for each institution are:

**Los Alamos National Laboratory:** Compare and contrast process/structure/property relations of multi-component, multi-phase advanced (high fissile density, U-based) ceramic fuel systems fabricated by both field assisted sintering and conventional sintering. TPOC and US Principle Investigator: Kenneth McClellan

**Idaho National Laboratory:** Spark plasma sintering, microstructural characterization and property optimization of high fissile density ceramic-based fuels. TPOC: Rory Kennedy

**Oak Ridge National Laboratory:** Thermodynamic and thermo-kinetic assessment of composite fuel interaction to inform advanced processing parameters. TPOC: Stewart Voit

**University of Florida:** Spark plasma sintering, microstructural characterization and property optimization of  $UO_2$ /nano-diamond fuels with enhanced thermal conductivity. TPOC: Jim Tulenko

Joint Research Center- Institute for Transuranium Elements: Adaptation of spark plasma sintering to plutonium environment for the comparison of oxide, nitride and carbide materials compaction using conventional press and sinter routes TPOC and EURATOM Principle Investigator: Joe Somers

In FY14 a first technical meeting was held at ITU. The US accomplishments included thermodynamic screening at ORNL of candidate composite ATF systems consisting of UN-USi<sub>x</sub> and UO<sub>2</sub>-UB<sub>x</sub>. Thermodynamically viable composites were identified for both systems. Initial experimental screening was performed at LANL on these systems demonstrating that the nitride-silicide systems require processing at higher currents than for the UO<sub>2</sub>-based composites but in both cases higher currents were relative to the single phase UO<sub>2</sub> reference case. ITU has successfully installed a spark plasma sintering system within a glovebox to enable exploring SPS processing of minor actinide-bearing fuels.

## **2.4 US/EURATOM and OECD Projects on Thermodynamics of Nuclear Fuels**

*T. M. Besmann, [besmannm@ornl.gov](mailto:besmannm@ornl.gov), S. L. Voit, ORNL; P. E. A. Turchi, LLNL; J. R. Kennedy, INL; R. J. M. Konings, ITU*

### **2.4.1 OECD-NEA Thermodynamics of Advanced Fuels-International Database (TAF-ID)**

Two different kinds of tasks were performed under the project:

- The introduction of existing models from different countries involved in the TAF-ID project. In some cases, several descriptions already exist for some of the chemical systems as for example, for the metallic fuels, for which models were developed in Japan (CRIEPI), in US (LLNL) and in France (CEA). In such a case, a choice had to be made as to which single description to use in the TAF-ID.
- The full assessment of chemical systems. Where there is no available model in the literature or coming from the countries involved in the project, a model had to be developed in the project on the basis of the available experimental data.

The current version of TAF-ID database contains the description of 178 binary and 47 ternary systems (Figs. 3, 4). The systems colored in blue are described from existing models published in the open literature. The systems in red were modeled by national participants in the TAF-ID project.

Ag-I Ag-Ti Ag-Zr  
 Al-Ca Al-Cr Al-Fe Al-Mg Al-O Al-Si Al-U Al-Zr  
 Am-Fe Am-Np Am-O\* Am-Pu\* Am-U Am-Zr  
 B-C B-Fe B-H B-I B-O B-Pu B-U  
 Ba-H Ba-I\* Ba-La\* Ba-Mo\* Ba-N Ba-O Ba-Ti\* Ba-V\*  
 C-Cr C-Fe C-Mo C-N C-Nb C-Ni C-O C-Pu\* C-Re C-Si C-Ta C-Ti C-U\* C-V C-W C-Zr  
 Ca-Fe Ca-Mg Ca-O Ca-Si Ca-U\* Ca-Zr\*  
 Ce-O\*  
 Cr-Cs\* Cr-Fe Cr-H Cr-I Cr-La\* Cr-Mo Cr-N Cr-Ni Cr-O Cr-Pu\* Cr-Si Cr-Ti Cr-U\* Cr-Zr  
 Cs-I\* Cs-Mo\* Cs-Nb\* Cs-O Cs-Pu\* Cs-Ta\* Cs-Te\* Cs-Ti\* Cs-U\* Cs-V\* Cs-Zr\*  
 Fe-Ni Fe-Np Fe-O Fe-Pu Fe-Si Fe-U Fe-Zr  
 Gd-O Gd-U\*  
 H-I H-O H-Sr  
 I-Mo I-Sr I-Te  
 La-Mo\* La-Nb\* La-O La-Pu\* La-Re\* La-Ta\* La-Te La-Ti\* La-U\* La-V\* La-W\*  
 Mg-O Mg-U\* Mg-Zr\*  
 Mo-N Mo-O Mo-Pd Mo-Pu\* Mo-Re Mo-Rh\* Mo-Ru Mo-Si Mo-Sr\* Mo-Te\* Mo-Ti Mo-U\* Mo-Zr  
 N-O N-Pu\* N-Si N-Ti N-U N-Zr  
 Nb-O Nb-Pu\* Nb-Si Nb-U Nb-Zr  
 Nd-O\* Nd-U\*  
 Ni-O  
 Np-O\* Np-Pu\* Np-U Np-Zr  
 O-Pu\* O-Ru O-Si O-Sr O-Te O-Th\* O-Ti O-U O-Zr  
 Pd-Rh Pd-Ru\* Pd-Te\*  
 Pu-Re\* Pu-Ru\* Pu-Si\* Pu-Ti\* Pu-U Pu-W\* Pu-Zr  
 Re-Si Re-U\* Re-W  
 Rh-Ru\* Rh-Te\*  
 Ru-Te\* Ru-U\*  
 Si-Ta Si-Ti Si-U\* Si-W Si-Zr  
 Sr-Ti\* Sr-V\*  
 Ta-U\*  
 Ti-U\* Ti-Zr  
 U-W\* U-Zr

Figure 3: Binary systems described in TAF-ID database

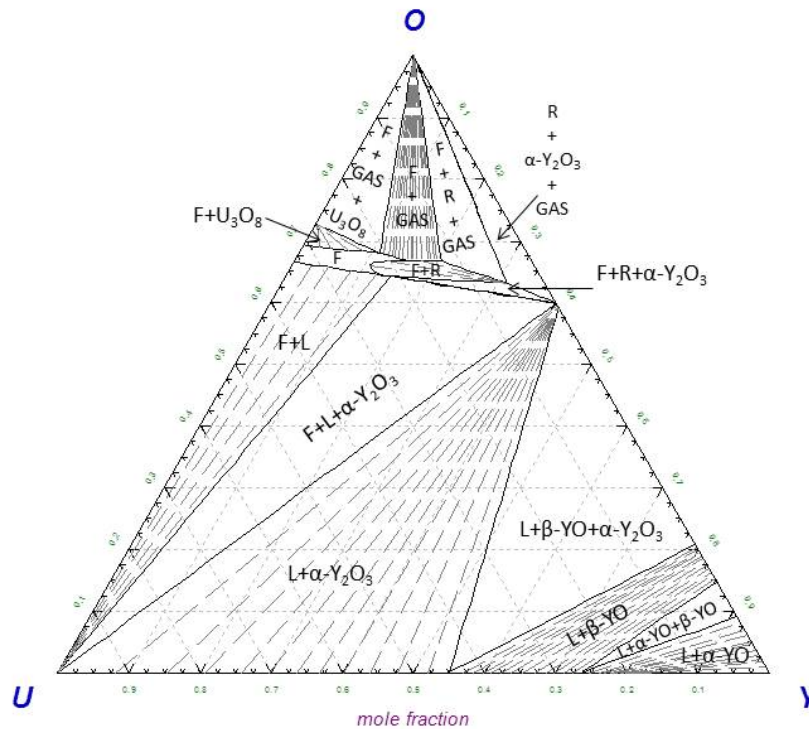
Al-Ca-O Al-Cr-O Al-Fe-O Al-Mg-O  
 Al-O-Si Al-O-U Al-O-Zr  
 Am-O-Pu  
 B-C-Fe B-Pu-U  
 C-Mo-Re C-Mo-Si C-Mo-Ti C-Mo-U C-N-Ti  
 C-O-Pu C-O-U C-Pu-U C-Pu-W C-Re-U C-Re-W  
 C-Si-Ti C-Si-U C-U-W C-U-Zr  
 Ca-Fe-O Ca-Mg-O Ca-O-Si Ca-O-U Ca-O-Zr  
 Cr-Fe-O  
 Fe-O-Si Fe-O-U Fe-O-Zr  
 Gd-O-U  
 La-O-U  
 Mg-O-Si Mg-O-U Mg-O-Zr  
 Nd-O-U  
 Ni-O-Si  
 O-Pu-U O-Pu-Zr O-Si-U O-Si-Zr O-U-Zr  
 Pu-U-Zr

Figure 4: Ternary systems described in TAF-ID database

## 2.4.2 I-NERI: Phase Equilibria and Thermochemistry of Fission Products in Urania Fuel

A representation for the thermodynamic properties and the phase equilibria of the U-Y-O system was created using the CALPHAD approach. To represent  $YO_2$  in the compound energy formalism for  $U_{1-y}Y_yO_{2+x}$ , the lattice stability was calculated using density functional theory. A

partially ionic liquid sublattice model is used for the liquid phase, and a Gibbs function for the stoichiometric rhombohedral phase  $UY_6O_{12}$  is proposed. The solid and liquid phases representing the binary U-O and Y-O models are used from Guéneau et al. [1] and Djurovic et al. [2] respectively. All available, self-consistent data was used for the optimization which resulted in coherent models for the U-Y-O system that are consistent across all databases used in the fuels program. An example of the results can be seen in the computed phase diagram of Fig. 5.



**Figure 5: Computed U-Y-O phase diagram at 1500K.**

#### References:

- [1] Guéneau, C. et al., Thermodynamic assessment of the uranium–oxygen system, *Journal of Nuclear Materials* 304 (2002) 161–175
- [2] Djurovic, D. et al., Thermodynamic modeling of the yttrium–oxygen system, *Computer Coupling of Phase Diagrams and Thermochemistry* 31 (2007) 560–566

Thermodynamic calculations were performed using the FactSage thermochemical software. The reactants were defined from the various binary systems, appropriate thermodynamic databases were selected, and the calculation determined equilibrium products and phases that satisfy the mass balance and minimize Gibbs energy.

The following temperature-dependent phase stabilities were computed for proposed two-phase composites, with 10 mol% second phase. Each two-phase composite is labeled with either a “✓” indicating that the combination passed the initial thermodynamic screening or an “✗” if it failed.

- |                                         |                                                        |                                                                    |
|-----------------------------------------|--------------------------------------------------------|--------------------------------------------------------------------|
| • UN – UB <sub>4/2</sub> ✓              | • U <sub>3</sub> Si <sub>5</sub> – UB <sub>4/2</sub> ✗ | • U <sub>3</sub> Si <sub>2</sub> – UB <sub>4/2</sub> ✗             |
| • UN – U <sub>3</sub> Si <sub>2</sub> ✓ | • UO <sub>2+x</sub> – UB <sub>4/2</sub> ✓              | • UN-10%U <sub>3</sub> Si <sub>5</sub> -<br>10%UB <sub>4/2</sub> ✓ |
| • UN – U <sub>3</sub> Si <sub>5</sub> ✓ |                                                        |                                                                    |

Shown in Figure 7 is a computed phase diagram for the UN-U<sub>3</sub>Si<sub>2</sub> system up to 2500°C. The phase assemblage for UN-10%U<sub>3</sub>Si<sub>2</sub> shows some USi formation between 300°-1575°C although the amount of USi is several orders of magnitude less than the primary phases and thus can be considered insignificant. Above 1658°C, liquid the U-Si-N phase replaces the silicide. The phase assemblage of UN-U<sub>3</sub>Si<sub>2</sub> remains stable over the temperature range of interest so this combination can be considered a viable composite fuel option from a thermodynamic standpoint.

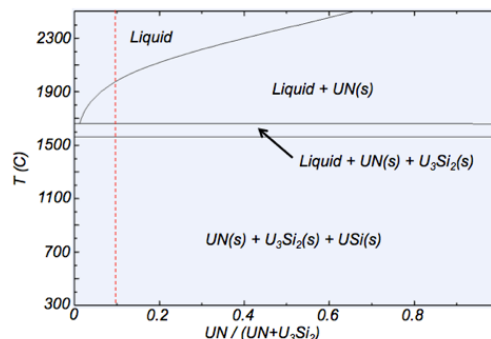
Also completed was a preliminary assessment of possible routes to synthesize feedstock materials for the ceramic composite fuels from uranium hexafluoride (UF<sub>6</sub>). This initial evaluation examines the thermodynamic possibility of combining UF<sub>6</sub> with a reactant to directly form various uranium borides or uranium silicides. The thermodynamic calculations for synthesis reactions over a wide temperature range produced the following results:

- Uranium silicides cannot be prepared from uranium fluorides plus silicon.
- UF<sub>6</sub> or UF<sub>4</sub> will react with boron to form UB<sub>12</sub>.
- UF<sub>6</sub> or UF<sub>4</sub> will not form the lower borides UB<sub>2</sub> or UB<sub>4</sub>.
- In addition, BF<sub>3</sub> will not react with UF<sub>6</sub> or UF<sub>4</sub>, and thus borides cannot be formed from BF<sub>3</sub>.

The next phase of this study will continue the thermodynamic assessment of the chemical compatibility of ceramic candidate systems with a closed system analysis of the two-phase composites that passed the initial screening evaluation and a more extensive analysis will be carried out to determine alternate routes for the synthesis of uranium nitride, boride, and silicide feedstock materials.

#### References:

- [1] Okamoto H., N-U (Nitrogen-Uranium), J. Phase Equilib., Vol. 18, 1997, p. 107.
- [2] Okamoto H., Si-U (Silicon-Uranium), Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski, Vol. 3, 1990, p. 3374-3375.
- [3] Mathews, R.B., et al., Fabrication and Testing of Uranium Nitride Fuel for Space Power Reactors, Journal of Nuclear Materials. 151, 1988, p 334-344.
- [4] Streit, M., et al., Nitrides as a nuclear fuel option, Journal of the European Ceramic Society 25, 2005, p. 2687-2692.



**Figure 7: Computed pseudo-binary phase diagram of the UN-U<sub>3</sub>Si<sub>2</sub> system.**



[5] Chevalier, P.Y., et al, Thermodynamic modeling of the N-U system, Journal of Nuclear Materials 280, 2000, p. 136-150.

[6] Hofman, G. L. and J. L. Snelgrove, 1994, "Dispersion Fuels," in Nuclear Materials, B. R. T. Frost (ed.), Weinheim, New York, Basel, Cambridge, Tokyo: VCH Publishers Inc., p. 45-108.

[7] Kaufman, Albert F., Nuclear Reactor Fuel Elements, Metallurgy and Fabrication, John Wiley & Sons. N.Y., 1962.

### **3.2 Screening of Accident Tolerant Fuel Candidate Systems: Reactor Performance and Safety Analyses**

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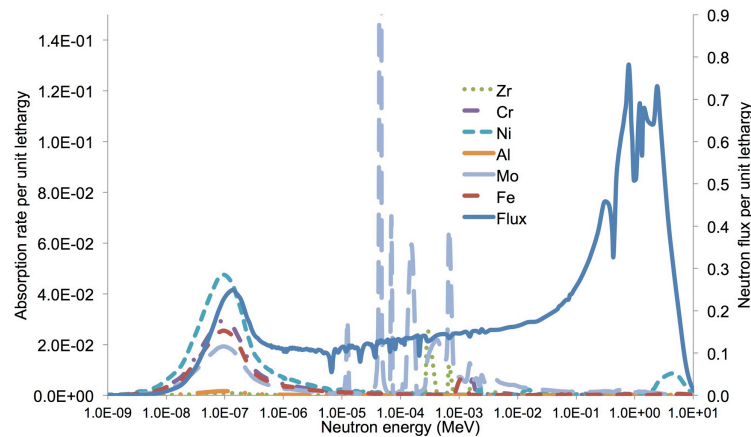
An assessment of the viability and potential attractiveness of advanced nuclear fuels must include consideration of how proposed concepts will impact the nominal reactor performance and safety characteristics of current commercial light-water reactors versus the reference  $\text{UO}_2\text{-Zr}$  system. In FY14 BNL conducted screening of several uranium nitride composite fuel concepts proposed by Los Alamos National Laboratory, Westinghouse, and others, where the uranium nitride is "shielded" from water by one or more secondary phases. The BNL assessments were performed in support of the Accident Tolerant Fuel Performance Metrics, namely: *"the assessment must address how implementation of the concept will affect reactor performance and safety characteristics"*. This highlight presents assembly-level screening calculations for UN- $\text{U}_3\text{Si}_5$  fuel concepts paired with several potential advanced cladding options. In addition, selected equilibrium core analysis results with thermal feedback are compared for  $\text{UO}_2$  and UN- $\text{U}_3\text{Si}_2\text{-UB}_4$  fuels. In this case, the  $\text{UB}_4$  content as a tertiary phase has been optimized to match the performance of an Integral Fuel Burnable Absorber (IFBA). We also present results from a transient analysis of a large break Loss-of-Coolant Accident (LB-LOCA) for  $\text{UO}_2$  and UN- $\text{U}_3\text{Si}_2\text{-UB}_4$ .

#### **3.2.1 ANALYSIS of "DROP-IN" FUEL FOR UN/ $\text{U}_3\text{Si}_5$ WITH Fe-BASED CLADDING**

Several advanced iron-based claddings are under consideration due to increased oxidation resistance versus zirconium-based cladding. We performed assembly-level neutronic analysis for a 17 x 17 PWR assembly with 4.9% enriched  $^{235}\text{U}$  to assess the impact of these advanced fuel and cladding materials on reactivity, safety coefficients, and cycle length/burn-up. The focus of this highlight is two commercial alloys: Kanthal AF and Kanthal APMT. The cladding thickness for the predominantly iron-based cladding materials was assumed to be 0.0419 cm versus 0.0572 cm for zirconium-based cladding. The fuel pellet radius was increased and the fuel-clad gap thickness was maintained versus zirconium cladding. Our analyses showed a reactivity penalty due to the proposed advanced claddings. In terms of cycle length, the reactivity penalty was compensated via the higher heavy metal loading and increased fuel pellet thickness of the UN- $\text{U}_3\text{Si}_5$  fuels, as shown in Table 1. Relative neutron absorption rates in various existing or proposed cladding constituent elements are shown in Figure 8. The element with the highest cumulative absorption rate is Mo, followed by Ni, Cr, Fe, Zr, and Al. The important take-away message of this study is that, if the fuels are feasible from the perspective of fabricability and performance, high density UN- $\text{U}_3\text{Si}_5$  fuels can overcome the reactivity penalty of several proposed cladding materials and are able to closely match  $\text{UO}_2\text{-Zr}$  cycle lengths.

**Table 1: Three-batch cycle length and discharge burn-up for various advanced fuel/cladding options at 4.9%-enriched  $^{235}\text{U}$ .**

Fuel/Clad	Primary phase content	Secondary phase content	Tertiary phase content	Cycle length (EFPD)	Discharge burn-up (GWd/t)
$\text{UO}_2$ - Zr	95.00%	0.00%	0%	532.9	61.6
UN - $\text{U}_3\text{Si}_5$ - Zr	50.00%	40.00%	0%	566.5	61.6
UN - $\text{U}_3\text{Si}_5$ - $\text{UB}_2$ - Zr	55.00%	34.50%	0.50%	524.4	55.2
UN - $\text{U}_3\text{Si}_5$ - AF	55.00%	35.00%	0%	533.1	52.2
UN - $\text{U}_3\text{Si}_5$ - APMT	55.00%	35.00%	0%	526.0	51.5
UN - $\text{U}_3\text{Si}_5$ - $\text{UB}_2$ - APMT	75.00%	14.50%	0.50%	510.5	44.5



**Figure 8: Relative neutron absorption rates in proposed cladding constituent elements.**

### 3.2.2 EQUILIBRIUM CORE ANALYSIS FOR UN- $\text{U}_3\text{Si}_2$ - $\text{UB}_4$

This example shows one role of core analysis with thermal feedback in the analysis of proposed candidate fuel/cladding combinations. This highlight explores a new proposed composite (UN- $\text{U}_3\text{Si}_2$ - $\text{UB}_4$ ) with a tertiary component ( $\text{UB}_4$ ) that has been tuned to match the performance of an assembly with 112 IFBA coated fuel rods. This type of configuration is relevant to a recent Westinghouse patent (7,139,360 B2). We compared several cases in a 17 x 17 assembly dimensions and an AP1000-like core: a nominal  $\text{UO}_2$ -Zr case with 112 IFBA coated rods, a UN/ $\text{U}_3\text{Si}_2$ -Zr case with 112 IFBA coated rods, a UN/ $\text{U}_3\text{Si}_2$ - $\text{UB}_4$ -Zr case with 5 concentric depletion zones (“rings”) per fuel pin. In the UN- $\text{U}_3\text{Si}_2$ - $\text{UB}_4$  case the same mass of natural boron from the 112 IFBA coatings is conserved, but is dispersed throughout all 264 of the fuel pins in the assembly as  $\text{UB}_4$ . The PARCS regulatory-grade core simulator was utilized in a full three-dimensional model of the reactor core including thermal-hydraulic/temperature reactivity feedback. Equilibrium cycle fuel shuffling was performed with the fresh assemblies located near the periphery of the core and the once- and twice-burned assemblies located throughout the central core region. Radial power peaking in the core at End of equilibrium Cycle (EOC) is shown in Figure 9 for  $\text{UO}_2$ -Zr and UN/ $\text{U}_3\text{Si}_2$ - $\text{UB}_4$ . Assembly-average fuel temperatures are shown in Figure 10. This analysis shows that this advanced composite fuel, even with burnable absorber integrated into the pin as a tertiary phase, can closely match the core performance of a nominal  $\text{UO}_2$ -Zr fuel. In addition, the fuel temperatures will be much lower due to the enhanced



thermal properties of the fuel. This shows how analyses like these can inform on the potential for changes to margins for a given candidate fuel system.

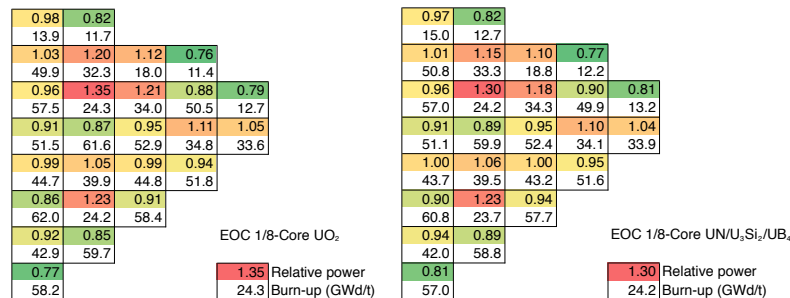


Figure 9 Radial assembly power peaking at EOC for an AP1000-like reactor core.

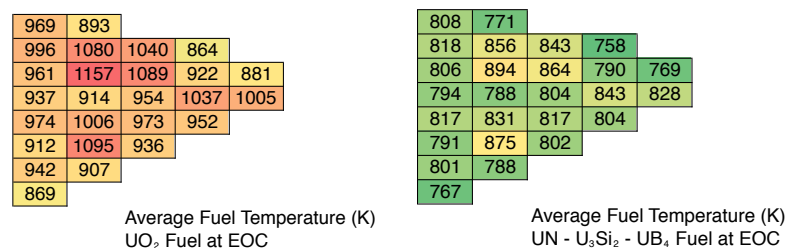
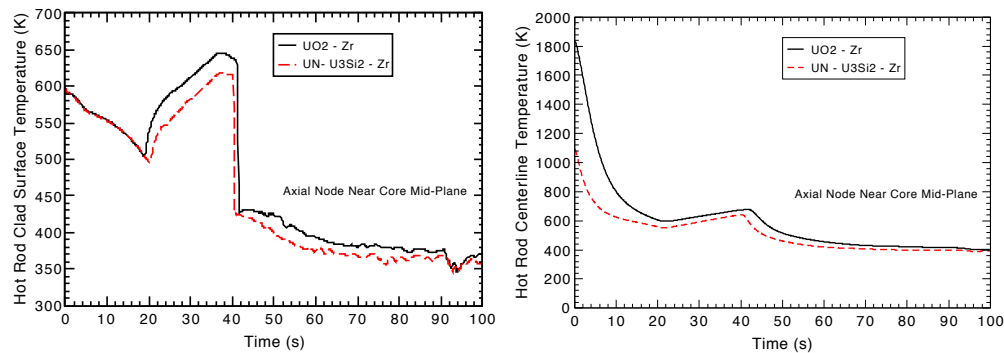


Figure 10 Assembly average fuel temperatures for an AP1000-like equilibrium reactor core at EOC.

## 3.2.3 TRANSIENT ANALYSIS OF A LARGE BREAK LOCA EVENT

This section demonstrates how transient safety analyses can inform on margins and timing to a safety limit. The focus of this example is a prediction of how UN/U<sub>3</sub>Si<sub>2</sub>/UB<sub>4</sub> composite fuel will perform in a Large Break Loss of Coolant Accident (LB-LOCA) event coincident with loss-of-offsite power. This primarily thermal hydraulic transient is evaluated using a detailed TRACE plant model based on a Westinghouse PWR with point-kinetics utilized for the reactor neutronics. The fuel response in the event depends on the thermophysical properties of the fuel, the fuel/clad/gap geometry and gap conductance, the system thermal hydraulics, and the neutronic feedback. The LB-LOCA is primarily a thermal hydraulic transient, and the initiating break and subsequent Emergency Core Cooling System (ECCS) flow dictate the peak clad temperature (PCT) in the event. A large break in the cold leg of primary loop 1 was simulated with a loss of off-site power coincident with the reactor trip. For this fast transient the thermal-hydraulics and fuel thermal properties dictate the overall response more so than the reactivity feedback. Figure 11 shows the PCT and fuel centerline temperature for the two fuel types. The PCT for the nitride fuel is ~30 K lower than the oxide fuel. Initially the nitride is much cooler than the UO<sub>2</sub>-Zr fuel, but the temperature difference decreases during the accident event cascade. Although the heat transfer properties of the UN-U<sub>3</sub>Si<sub>2</sub> fuel are improved, the decay heat of the reactor and the heat removal capability of the ECCS are key boundary conditions for the transient fuel temperature response.



**Figure 11: Hot rod clad surface temperature (left) and hot rod centerline temperature for LB-LOCA event in  $\text{UO}_2$  and  $\text{UN-U}_3\text{Si}_2$  fuelled PWRs.**

### 3.3 Uranium silicide fuel phases: Assessment of thermophysical properties, oxidation behavior and cladding compatibility

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The uranium-silicon binary system possesses a range of compounds that have been historically investigated and utilized to a limited extent as nuclear reactor fuels. Of the multiple compounds,  $\text{U}_3\text{Si}$  and  $\text{U}_3\text{Si}_2$  are most familiar; their high uranium densities have made them an intriguing choice for incorporation into composite plate fuels in research reactors and other low power core redesigns where retained neutronic performance was desired at lower enrichments. This increased uranium density compared with uranium dioxide ( $\text{UO}_2$ ) has made them attractive to a new generation of nuclear fuels research driven by the renewed push for accident-tolerant fuels (ATF) for use in existing and Gen III+ light water reactors (LWR). An increased uranium density may facilitate incorporation of cladding variants that incur a neutronic penalty compared to the zirconium cladding alloys used currently. Performance gains may also be realized through advancement of composite fuel designs that aim to incorporate oxidation resistant phases into the fuel/cladding system in order to increase coping time during a loss-of-coolant accident (LOCA), *e.g.* see the BNL highlight on screening of ATF systems via reactor performance and safety analyses.

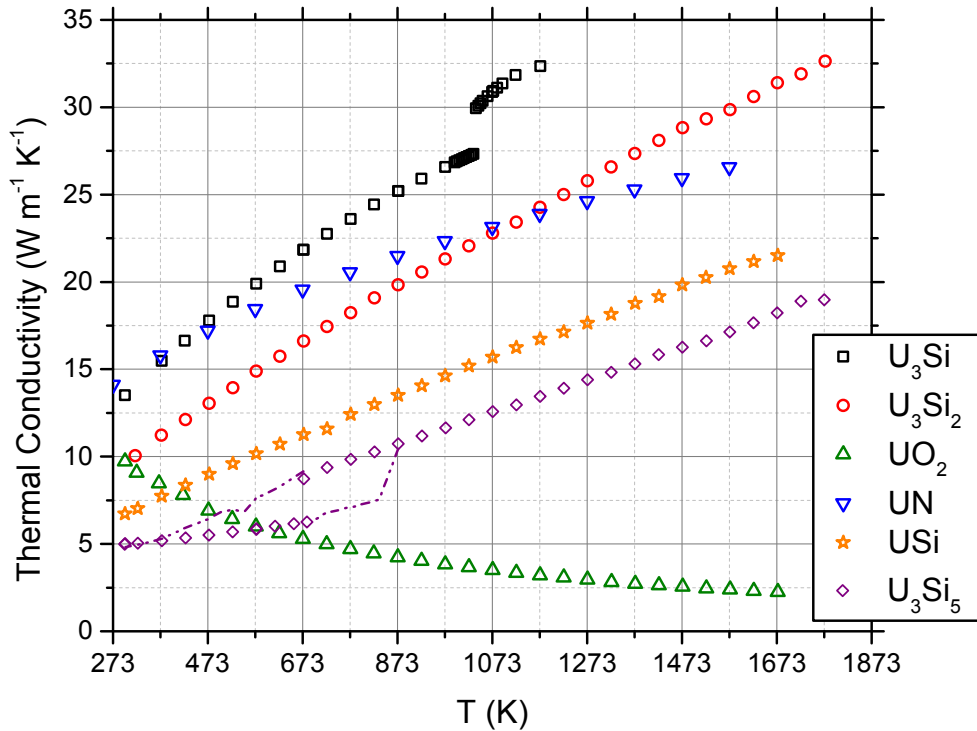
The importance of temperature in governing many aspects of reactor performance demands knowledge of thermophysical properties from room temperature to anticipated operating conditions and through temperatures brought about by potential transients. Even the more familiar U-Si compounds  $\text{U}_3\text{Si}$  and  $\text{U}_3\text{Si}_2$  have received minimal attention with respect to their thermophysical properties at elevated temperatures. An experimental campaign was undertaken in FY14 to provide thermophysical and oxidation data and facilitate the evaluation of potential of U-Si compounds for LWR applications. Monolithic specimens for thermal conductivity and oxidation testing were prepared by arc melting high purity feedstocks of depleted U and Si. Resulting buttons were comminuted, pressed and sintered to desired geometries using standard powder metallurgical routes in a W-metal furnace. X-ray diffraction (XRD), scanning electron microscopy (SEM), and chemical analyses were conducted to verify the composition of U-Si specimens to be phase pure within acceptable limits.

The results of thermal conductivity measurements performed from room temperature to the melt points of the four U-Si binary compounds investigated are shown in Figure 12. Reference data for  $\text{UO}_2$  and UN are included for comparison. The conductivity for each of the U-Si compounds increase with temperature, and are generally greater in value than  $\text{UO}_2$  at LWR

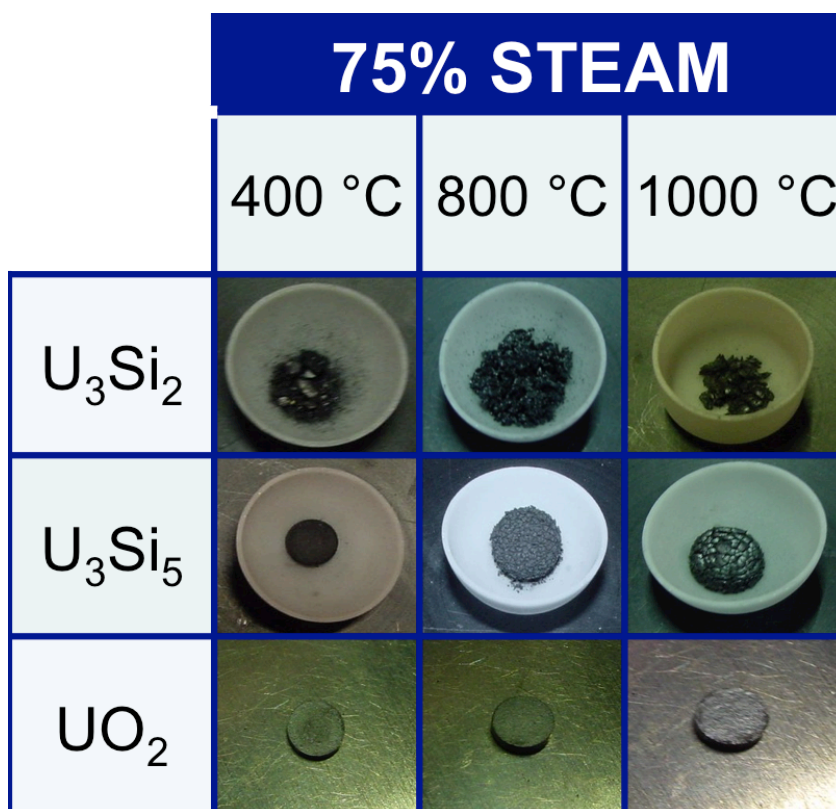
operating temperatures. Early reports of a martensitic phase transformation in  $U_3Si$ , which have recently been discounted in the literature, were confirmed in all of the thermophysical measurements. Characterization of the high temperature  $\delta'$ - $U_3Si$  thermophysical properties was also determined for the first time and published in the *Journal of Nuclear Materials*. Results for  $U_3Si_5$  exhibit a low temperature reaction that has not been measured previously in the literature. Properties for  $U_3Si_5$  have been accepted for publication in the *Journal of Nuclear Materials*. These data have been transmitted to collaborators at INL, BNL, and WEC to facilitate design of ATF-1 irradiation experiments to be performed at the Advanced Test Reactor in the coming year.

Oxidation testing was conducted on U-Si compounds in air and steam environments to simulate performance under ambient storage and LOCA conditions, respectively. U-Si compounds,  $UO_2$ , and UN that are exposed to air at elevated temperature degrade to a black powder. This effect is not observed until above 250 °C, which is above the temperature where UN degrades. Macroscopic photographs of  $U_3Si_2$  and  $U_3Si_5$  compared to  $UO_2$  after isothermal holds under 75%- $H_2O$ /Ar atmospheres are shown in Figure 13.  $U_3Si_2$  fragmented under all test conditions,

while  $U_3Si_5$  exhibited some evidence of mechanical integrity.  $UO_2$  pellets gained mass under the test conditions, but did not degrade after exposure to steam. Further isothermal testing on  $U_3Si_5$  in 75% steam/Ar reveals that U predominately oxidizes in the initial stages followed by retarded oxidation of the Si. This work suggests that minimal improvement in the oxidation performance of LWR fuels would be attainable by inclusion of the two U-Si compounds investigated.



**Figure 12: Thermal conductivity of U-Si binary compounds as a function of temperature to the melt points of the various compounds. Values are compared to reference data for  $UO_2$  and UN.**



**Figure 13: Macroscopic photographs of specimens after exposure to steam at a variety of temperature.**

A matrix of candidate accident tolerant fuels along with  $UO_2$  paired with candidate cladding materials underwent varied thermal profiles to both screen general fuel/cladding compatibility as well as to investigate the formation of secondary phases that could induce pellet-cladding chemical interactions during reactor service. An assembly was designed to maintain intimate contact between the pellet and the cladding sample at temperatures below

1300 °C. The test assembly consists of an outer stainless steel tube fixed with Swagelok fittings on both ends. This complete containment serves to limit the spread of liquid phases that may form as a result of inter-diffusion. A steel spring fixed in length to provide 3 MPa of load upon the assembly closure at room temperature maintained the contact between the fuel pellet and cladding through the experiments.

No significant reactions were observed following exposure for temperatures up to 1000 °C and time intervals up to 100 h. Compatibility was generally good for the couples tested. Formation of a U-Al-O phase appears to be a possibility for  $U_3Si_2$  and Fe-Cr-Al alloys. Furthermore, qualitative investigation suggests that  $U_3Si_2$  may getter oxygen more effectively than candidate Fe-Cr-Al materials. This dramatic reversal from the operational experience of  $UO_2$  and a zirconium alloy cladding, in which the cladding oxidizes much more readily than the fuel, is likely to have significant impact on how a reactor fuel responds to either a cladding breach during normal operation or possible transients. Finally, the stability of both uranium silicide and uranium nitrides fuels and SiC cladding is in question based upon thermodynamic calculations. Ongoing experimental work will investigate the kinetics of these reactions to evaluate the potential design impact.

### **3.4 Understanding and Improving the Carbothermic Reduction/Nitridization Route for UN Synthesis**

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Uranium mononitride (UN) has been historically of interest as a nuclear fuel due to its high actinide density, high melting point, and high thermal conductivity. Although traditionally considered for fast reactor and transmutation fuels, its favorable attributes have made it a candidate for a constituent in ceramic composite accident-tolerant fuels (ATF) for light water reactor (LWR) service. For example UN-U<sub>3</sub>Si<sub>2</sub> composite fuel is a system being investigated under the Westinghouse-led FOA project. In addition to superior thermophysical properties that will reduce fuel centerline temperatures thereby minimizing restructuring and fission product transport, its candidacy is driven by its high uranium density (40% greater than uranium dioxide), which could facilitate replacement of zirconium claddings with stainless steel without a large penalty to reactor operation, *e.g.* see the BNL highlight on screening of ATF systems via reactor performance and safety analyses. One of the multiple research pathways necessary to advance UN as an LWR fuel option is an improved understanding of the thermodynamic drivers that will govern the chemistry and structure of UN feedstock. These characteristics dictate the structure-property relationships of dense fuel product and in-pile performance.

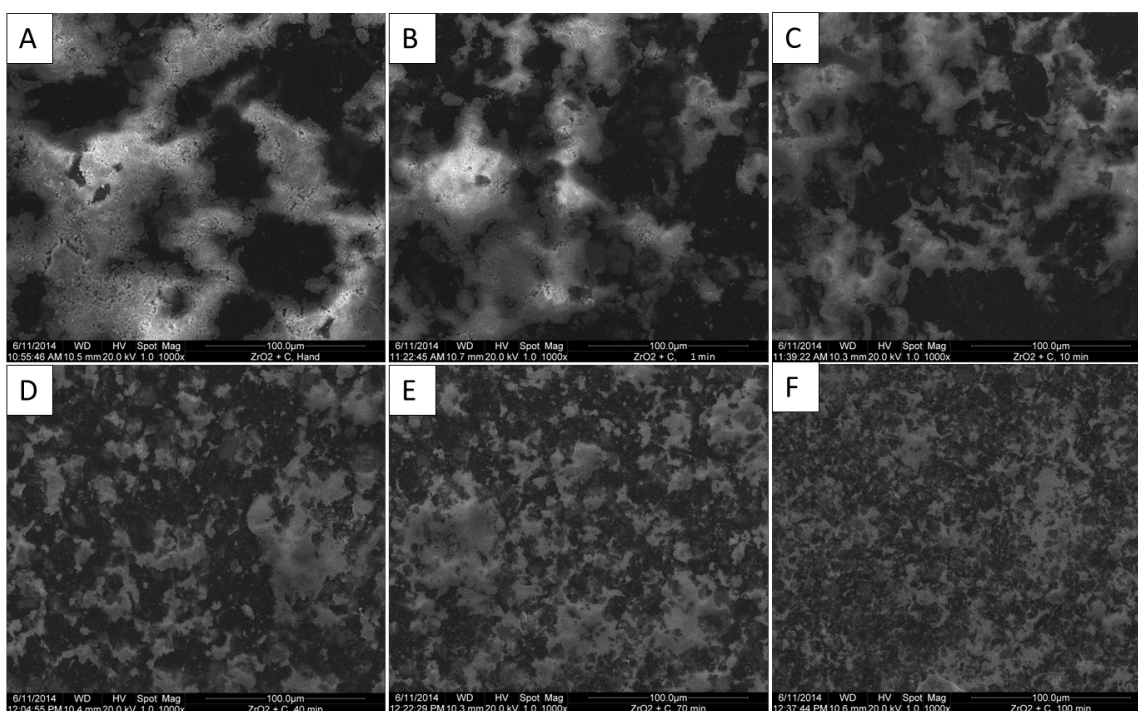
The carbothermic reduction/nitridization (CTR-N) route has been extensively utilized to synthesize bulk UN. This process uses uranium dioxide/carbon pressed pellets as the starting material and molecular nitrogen as the nitriding agent. This route was chosen because it is assumed to be the UN fabrication route most amenable to immediate industrial scale processing. Although conventional wisdom suggests that a fuel which incorporates UN will require a MOX-like glovebox line during fabrication, there has been recent evidence that the CTR-N process has the potential to be conducted at existing UO<sub>2</sub> fabrication plants with only minimal changes to standard processing procedures. This process has been employed extensively at LANL for synthesis of UN for multiple programs at kilogram levels. However, the precise time-temperature-atmosphere profiles have underwent minimal optimization over the years. While legacy conditions have been found suitable to yield a product of acceptable impurity levels, the precise rate limiting factors that dictate purity are not well understood. These must be assessed not only to improve both the product and efficiency of laboratory scale synthesis, but also to evaluate future industrial feasibility and costs.

This CTR-N process is currently being studied using ZrO<sub>2</sub> as a surrogate material instead of radioactive UO<sub>2</sub>, because this allows greater freedom in material handling during the initial investigations. A full systematic study of the UO<sub>2</sub> CTR-N process will begin near the transition to FY15. The current effort focuses largely on the coupling of thermogravimetric analysis (TGA) and quadrupole mass spectrometry (QMS). TGA is capable of measuring the mass changes associated with competing mass loss (evolution of carbon monoxide) and mass gain (addition of nitrogen) mechanisms. Synchronized QMS allows one to differentiate between these mass gain and mass loss mechanisms, resulting in kinetics information for these individual reactions. The material is also being analyzed using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis will give information on the relative phase abundance as the oxide transitions to the carbide, to a mixed carbonitride, and finally to the nitride. The SEM analysis will grant information on the microscopic physical changes as they occur during the CTR-N reaction.

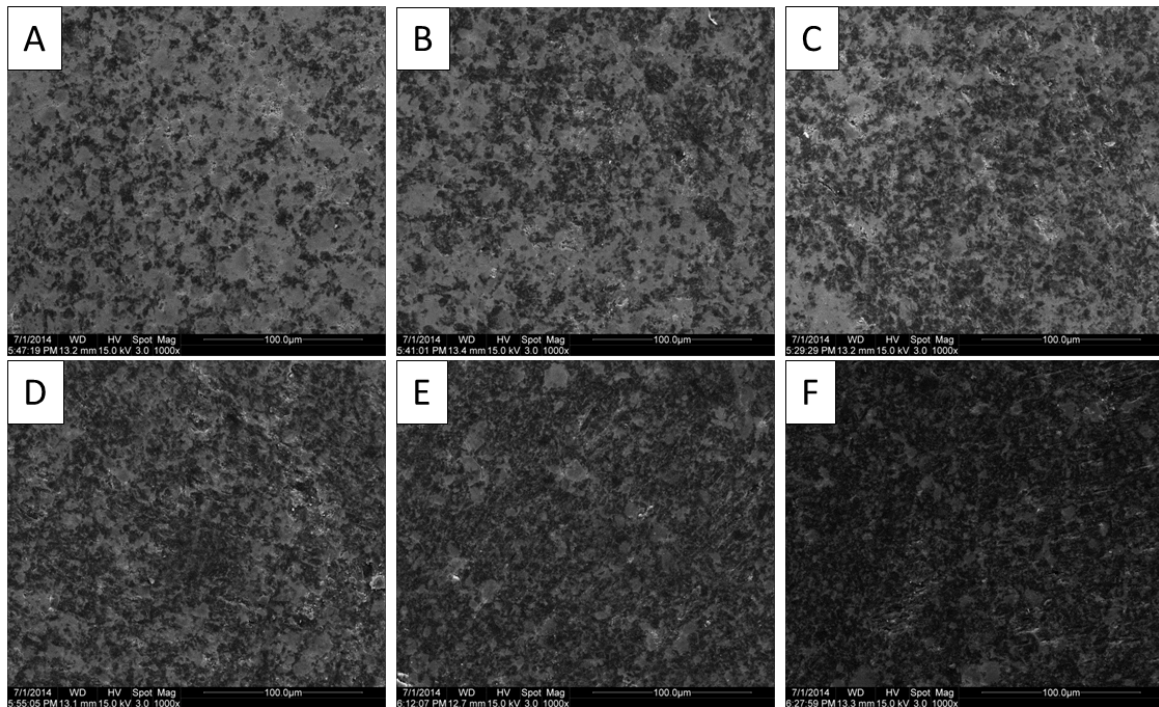
Initial findings using ZrO<sub>2</sub> surrogate material have demonstrated the importance of feedstock morphology on the resulting kinetics of nitride formation. Strong evidence has been found that



variables such as starting particle size, particle shape, and milling time play significant roles in the conversion from oxide to nitride. Figures 14 and 15 show the effects that milling time and starting C:O ratio have on the starting morphology of the feedstock. It was found that the reduction portion of the CTR-N reaction has a squared dependence on milling time. This squared dependence is a result of the material being fractured during the milling process, thus increasing the starting contact area between the  $\text{ZrO}_2$  and the graphite. However, it remains unclear how this greater starting contact area will affect the availability of nitrogen to the interior bulk material, as the nitrogen requires a pathway to the interior which is diminished as the material is homogenized. The starting C:O ratio was also found to be important in engineering this reaction. It was found that a C:O ratio of 2.5 provided the most rapid reduction. Again, it remains to be seen how this will affect the conversion to nitride or the ability to produce a high purity material.

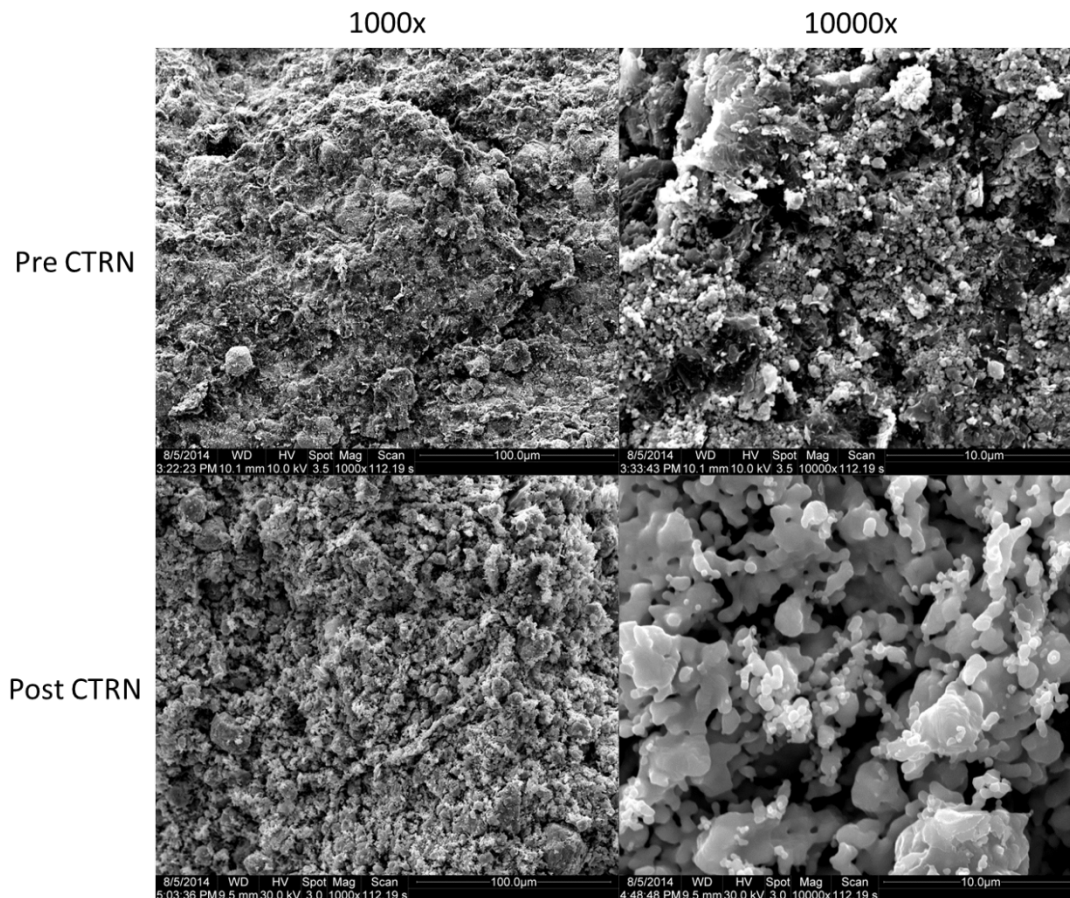


**Figure 14: The effect of milling time on starting morphology for  $\text{ZrO}_2$ -graphite mixtures. Homogenization is seen to occur as milling time increases. The C:O ratio was 1.5. [A) hand milled, B) 1 min Spex mill, C) 10 min Spex mill, D) 40 min Spex mill, E) 70 min Spex mill, F) 100 min Spex mill]**



**Figure 15: The effect of C:O ratio on starting morphology for ZrO<sub>2</sub>-graphite mixtures. The milling time was 100 minutes. [A) C:O of 0.5, B) C:O of 1.0, C) C:O of 1.5, D) C:O of 2.0, E) C:O of 2.5, F) C:O of 3.0]**

Effects such as pore formation and sintering are believed to play major roles in not only the conversion rate, but also in the purity of the final material. It therefore becomes critical to understand the effect that the microstructure has as the reaction progresses so that the process may be engineered and optimized for industrial use. Figure 16 shows the changes to the microstructure that take place during the conversion to nitride. It appears that all graphite is essentially transformed into pores/channels which provide the nitrogen access to the bulk material. This stresses the importance of understanding the starting morphology as shown in the two previous figures. The interplay between all of these variables is complex, but it is in the process of being understood.



**Figure 16: Scanning electron microscope (SEM) image of zirconium oxide mixed with graphite before the CTR-N reaction (top), and the material after the CTR-N reaction (bottom). Notice the pore formation and sintering that took place during the reaction. Reaction temperature was 1425 °C, milling time was 100 minutes, and C:O ratio was 1.5.**

The ultimate goal of this project is to determine the order, timing, and kinetics of the transition from oxide to carbide, to carbonitride, and finally to nitride as the CTR-N reaction progresses. This will allow process variables such as temperature and atmosphere to be adjusted at the precise time needed for optimized conversion. The figure shown below (Figure 17) plots the reaction rate as a function of reaction progression for several temperatures and atmospheres. The reaction rate and progression are determined by measuring the competing mass changes mentioned above using TGA. This gives information on the rate limiting mechanisms as well as the nature of the progression of these reactions during the CTR-N process. Perhaps most striking is the “hump” seen near the 79% mark, which likely corresponds to the onset and progression of the conversion of carbide or carbonitride to nitride. There also appears to be a change in reaction mechanism near the 98% mark, possibly corresponding to the onset of carbonitride formation. These and similar hypotheses are currently under investigation. The kinetic detail elucidated in these studies provides the tools necessary to understand and optimize the synthesis of high purity UN. This level of understanding is critical for facility and process design should this process be implemented on an industrial scale.



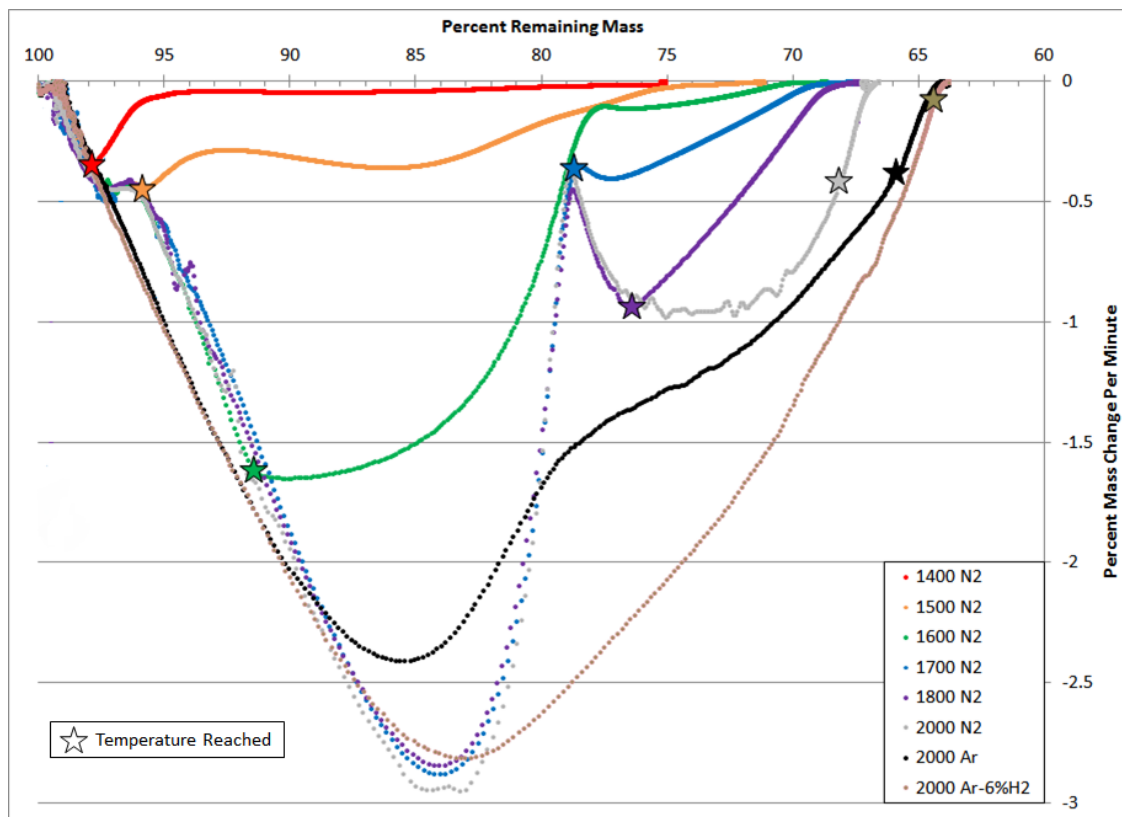


Figure 17: Zirconium oxide was mixed with graphite and allowed to react in a nitrogen atmosphere for temperatures between 1400 and 2000 °C. This material was also reacted in nitrogen, argon, and argon-6% hydrogen at 2000 °C. Ramp rate was 20 °C/min.

### 3.5 Thermo-mechanical Properties of Urania with Additives to Tailor Microstructure and Properties

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In the area of Advanced Accident Tolerant Ceramic Fuel Development, the majority of the FY14 effort focused on composite fuel seeking transformational R&D but some effort continued on incrementally advancing fuel technology, e.g. relatively minor modifications to  $\text{UO}_2$  to enhance properties that would yield benefit in accident tolerant behavior.

Small concentrations of oxide additives have been shown to improve the mechanical and physical properties of  $\text{UO}_2$  and provide avenues to control its microstructure. Hence, hardness, fracture toughness, and yield strength have been probed in samples containing small concentrations of various oxide additives at temperatures up to 1200 °C. Vickers indentation is used as a screening technique to determine which additives may enhance

$\text{UO}_2$  for reactor applications. The additives used in this study include:  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Y}_2\text{O}_3$ . Concentrations range between 0.05 and 0.2 wt%, depending on the additive type. The high temperature indentation experiments were performed at ASU on an indentation assembly capable of doing 1kgf indents at temperatures up to 1200°C.

Initial work focused on analyzing the microstructure of each sample to characterize the effects of the additives on grain size. The average grain diameter was calculated using

Orientation Imaging Microscopy (OIM<sup>TM</sup>) analysis or through the linear-intercept

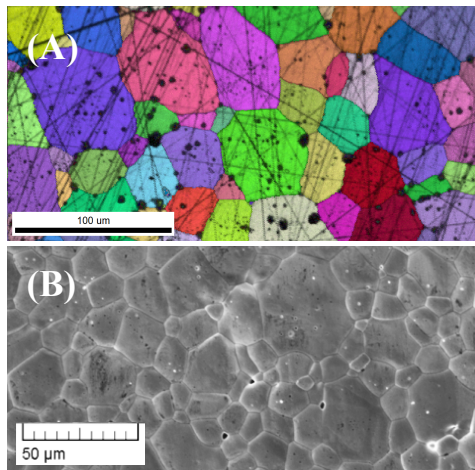
method from Scanning Electron Microscopy (SEM) pictures. Results are given in Table 2. Adding Al<sub>2</sub>O<sub>3</sub> resulted in an average grain diameter 24% smaller than the un-doped sample. Cr<sub>2</sub>O<sub>3</sub> additions did not lead to a noticeable change in average grain diameter. A bi-modal

microstructure occurred in the Cr<sub>2</sub>O<sub>3</sub>-doped samples, i.e., there was a high number of larger grains surrounded by smaller ones, which differs from the equiaxed grains seen in other samples. This can be seen in Figure 18. SiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>-doping did not yield any meaningful changes in average grain size. TiO<sub>2</sub>-doping led to an average grain diameter more than double what was seen in the un-doped sample.

**Table 2: Grain diameter (with average deviation) of UO<sub>2</sub> samples containing oxide additives.**

Additive	Avg. Diameter (μm)	Additive	Avg. Diameter (μm)
No Additive	13 ± 1	0.1 wt% Al <sub>2</sub> O <sub>3</sub>	9.8 ± 0.5
0.1 wt% Cr <sub>2</sub> O <sub>3</sub>	12 ± 1	0.2 wt% Al <sub>2</sub> O <sub>3</sub>	9.8 ± 0.7
0.2 wt% Cr <sub>2</sub> O <sub>3</sub>	15 ± 2	0.1 wt% SiO <sub>2</sub>	12 ± 1
0.1 wt% TiO <sub>2</sub>	26 ± 1	0.2 wt% SiO <sub>2</sub>	11.5 ± 0.7
0.2 wt% TiO <sub>2</sub>	28 ± 1	.05 wt% Y <sub>2</sub> O <sub>3</sub>	12.0 ± 0.3
		0.1 wt% Y <sub>2</sub> O <sub>3</sub>	12.1 ± 0.6

Vickers hardness at each temperature was determined from a direct measurement of the indent size. Across a temperature range of 450-1200 °C, the hardness of samples containing Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was not significantly different from the un-doped sample. Cr<sub>2</sub>O<sub>3</sub>-doping produced samples that were 15-20% harder than the un-doped sample at temperatures above 500°C. TiO<sub>2</sub>-doping yielded samples that were 17% harder at 500°C, and twice as hard at 1200°C. These results are shown in Figure 19. Experiments are still underway to form a more comprehensive picture of each sample's hardness at 100° C temperature intervals.



**Figure 18: A) OIM map of a 0.2 wt% TiO<sub>2</sub>-doped sample. B) Bi-modal microstructure seen in a 0.2 wt% Cr<sub>2</sub>O<sub>3</sub>-doped sample.**

Fracture toughness has been calculated only at room-temperature using equations empirically established by Niihara and Morena for brittle cracking due to Vickers indentation<sup>(1)</sup>. High-resolution imaging and measurement of the cracks is done using SEM. Al<sub>2</sub>O<sub>3</sub>-doped samples show a fracture toughness over 20% higher than the un-doped sample. The sample doped with 0.1 wt% Y<sub>2</sub>O<sub>3</sub> showed a 10% increase in

fracture toughness. The rest of the dopants led to samples with decreased fracture toughness at room temperature. Determining the fracture toughness at elevated temperatures is currently underway.

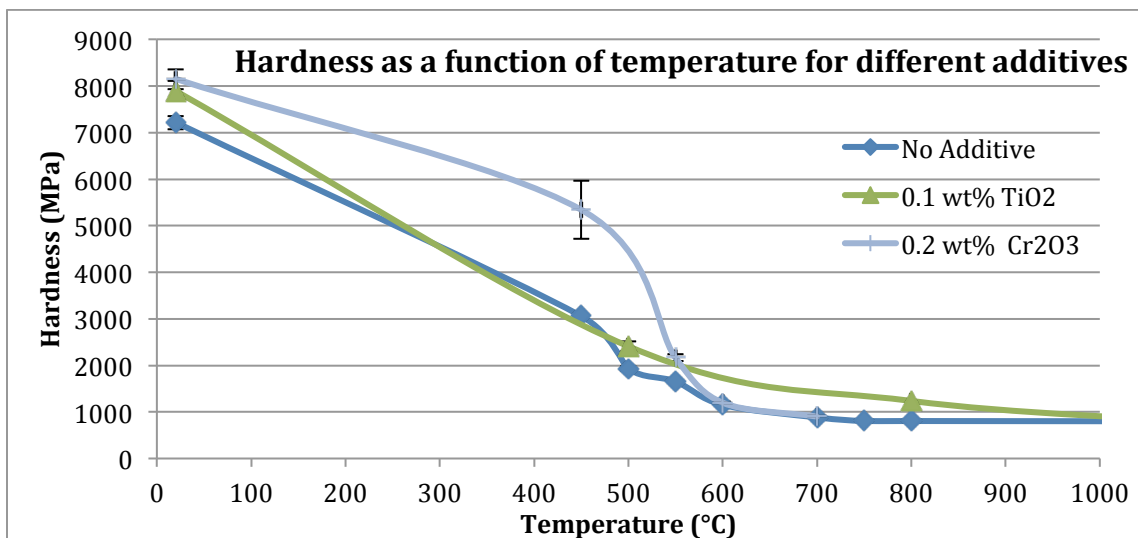


Figure 19: Vickers hardness for the 0.1 wt% TiO<sub>2</sub>-doped and 0.2 wt% Cr<sub>2</sub>O<sub>3</sub>-doped samples. The other additives types did not cause substantial changes in hardness.

Yield strength can be calculated in the high-temperature regime by measuring the extent of material pile-up around each indent. The pile-up area is measured using an optical profilometer, and yield strength is calculated from equations established by Giannakopoulos and Larsson<sup>(2)</sup>. Experiments are still in progress to determine how each additive alters the yield strength at high temperatures.

#### References:

- (1) K. Niihara, R. Morena. "Evaluation of  $K_{IC}$  of brittle solids by the indentation method with low crack-to-indent ratios," J. Mat. Sci. Letters 1 (1982) pp. 13-16.
- (2) A. Giannakopoulos, P. Larsson. "Analysis of Vickers indentation," Int. J. Of Solids Structures Vol. 31 No. 19 (1994) pp. 2679-2708.

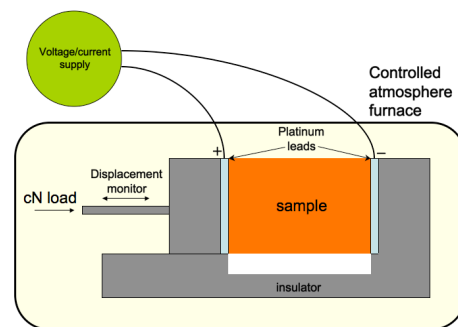
## 4. Reference Material and Technique Development

### 4.1 An Assessment Of The Field Assisted Sintering Technique Applied To Ceramic Fuel Constituents

J.A. Valdez, [javaldez@lanl.gov](mailto:javaldez@lanl.gov), D.D. Byler and K.J. McClellan, LANL

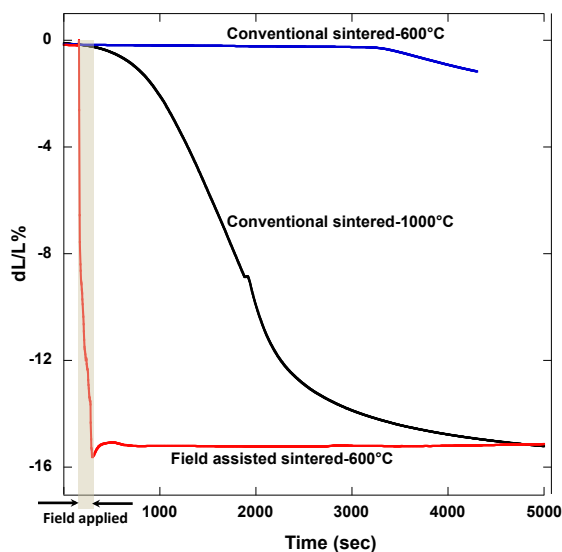
Flash sintering is a fairly new technique in the material processing field in which an electric field (DC or AC) is applied to a ceramic at either the onset of heat up or at an isothermal temperature that causes ultra fast sintering at temperatures hundreds of degrees below conventional temperatures. For example in wide band gap insulators such as zirconia, ultra fast sintering at low temperature has been shown in work by Downs et al. [1] in which they sintered YSZ to high density at 390°C using an applied field of 2250 V/cm. For comparison, typically zirconia is sintered at ~ 1400°C using conventional pressureless sintering. There are many examples of materials such as ionic conductors, electronic conductors, semi-conductors and insulators that have been flash sintered and possible mechanisms responsible for this effect have been proposed.

Typically a flash sintering apparatus consists of a furnace and power supply with leads in contact with a sample for application of the electrical field. Sample sintering is tracked either by a camera (image analysis is performed to calculate shrinkage) or a linear variable displacement transducer (LVDT). The simplicity and low cost, of this technique makes it adaptable

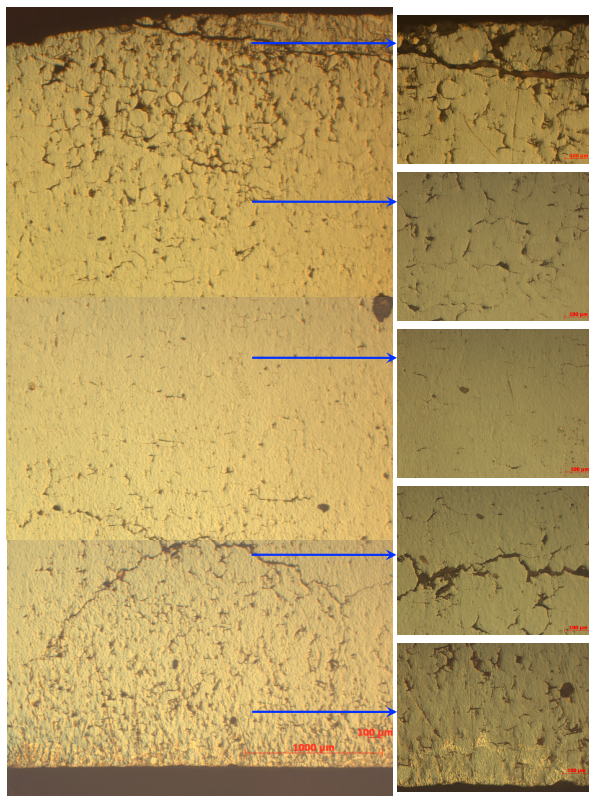


**Figure 20: Schematic representation of the LANL's flash sintering apparatus.**

to production settings as well as laboratory environments. Regarding flash sintering as applied to nuclear fuels, it may be used either as an initial processing step to increase green pellet strength or as an actual sintering step depending on the requirement. A schematic representation of a typical flash sintering apparatus, with the key components labeled is shown in Figure 20.



**Figure 21: Sintering strain ( $dL/L_0\%$ ) obtained from  $UO_{2.16}$  comparing FAS sintering at 600°C conventional sintering at 600°C and 1000°C.**



**Figure 22: Optical image of a cross-sectioned  $\text{UO}_{2.16}$  pellet**

that is 40% lower than the temperature required to achieve similar linear shrinkage using conventional sintering.

The resulting microstructure of a  $\text{UO}_{2.16}$  pellet that was sintered using the flash method can be seen in Figure 22. The micrograph shows a density gradient consisting of lower density regions on the pellets ends and a high-density region in the middle of the pellet. Experiments using longer hold times have been shown to produce increased pellet geometric uniformity, therefore it should be possible to produce a uniform microstructure throughout the pellet with optimization of the processing parameters, mainly temperature, power-density and hold time. Experiments were also performed on  $\text{UO}_{2.00}$ , the results from these experiments showed that  $\text{UO}_{2.00}$  also densifies at higher rates and lower temperatures compared to conventional sintering. Although the final density was lower in  $\text{UO}_{2.00}$  using identical parameters that produced higher final density in  $\text{UO}_{2.16}$ .

Several other flash sintering experiments were performed on matrix and constituent phases, both individually and as composites. To assess the flash sintering response of the previously mention materials, the parameter envelope used was that developed and optimized to achieve high final densities in  $\text{UO}_{2.16}$ . A summary of the experimental findings is shown in Table 3. The table shows densification using flash sintering was achievable in 8-YSZ (used to compare with literature values),  $\text{UO}_{2.16}$ ,  $\text{UO}_{2.00}$ , and  $\text{UO}_{2.00}\text{-UB}_2$  (localized) whereas using the parameters that produce densification in the previously stated materials showed no measurable densification in  $\text{UB}_2$ , UN,  $\text{U}_3\text{Si}_5$ , or  $\text{UN-U}_3\text{Si}_5$  composites.

This configuration was the basis of the flash sintering setup LANL developed and used to complete an assessment of advance field-assisted sintering techniques for ATF fabrication, which was focused on surveying urainia and ATF composites  $\text{UO}_{2.00}\text{-UB}_2$  and  $\text{UN-U}_3\text{Si}_5$ . The sintering that occurs at lower temperatures when using flash sintering takes place at ultra fast sintering rates (nearly instantaneously) as compared to conventional sintering; sintering occurs in seconds rather than hours. Our studies on  $\text{UO}_{2.16}$  showed that flash sintering produces comparable densities to those that are achievable using conventional sintering although at lower temperatures and much less time. This observation is shown in Figure 21. Specifically it shows that when using flash sintering the linear shrinkage that results in a final density of ~93% theoretical takes place in 3200% less time and at a temperature



**Table 3 FLASH sintered materials surveyed**

<b>Material system</b>	<b>Flash sintering densification</b>	<b>Comment</b>
8 YSZ (yttria stabilized zirconia)	yes	Densification less than reported in literature, most likely due to geometric effects.
UO <sub>2.16</sub>	yes	Good densification
UO <sub>2.00</sub>	yes	Excellent densification
UB <sub>2</sub>	no	Poor densification
UN	no	Poor densification
UO <sub>2.00</sub> -UB <sub>2</sub>	yes	Localized densification
UN-U <sub>3</sub> Si <sub>5</sub>	no	Poor densification

With the lack of densification in the previously stated materials, these material systems might be candidates for experiments using other field assisted sintering (FAS) techniques such as spark plasma sintering (SPS). The concept of investigating other FAS techniques on composite systems surveyed under this work package will be presented to both our jointly funded collaborators at the University of Florida studying SPS (Nuclear Energy University Programs (NEUP)) and the US/EURATOM (United States/European Atomic Energy Community) I-NERI project (International Nuclear Energy Research Initiative) investigating FAS techniques. Additionally, there also exists the possibility of achieving high densification using flash sintering in the proposed ATF composites and end-member phases by broadening the processing parameter envelope through more detailed studies performed by LANL.

#### References:

[1]A. Downs, V.M. Sglavo, "Electric field assisted sintering of cubic zirconia at 390°C", J Am Ceram Soc 2013; 96:1342–4.

## **4.2 Advanced Nondestructive Examination Techniques Development and Path to A-PIE of ATR Irradiated Fuels**

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The current “science based” approach to developing and testing new fuel forms requires that innovative and new techniques be developed and refined to extensively characterize nuclear fuel materials before, during and after irradiation to record and understand the microstructural and chemical evolution that occurs in the fuels during irradiation. The results from this characterization can produce data that is targeted to bridge the gaps in the current data sets to be used for improved predictive models and simulation and further aide in fuel development efforts. These efforts can effectively be used to streamline and advance the fuel licensing process to meet the needs of the nuclear fuels community and the path set forth by DOE to meet future nuclear power needs.

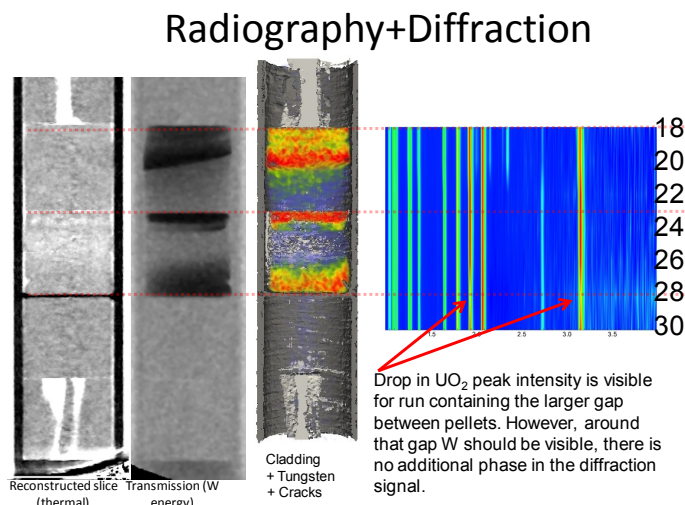
The emphasis of the current work is to develop, assess and demonstrate advanced non-destructive evaluation (NDE) techniques in support of advanced post irradiation examination (A-PIE) efforts on fresh and irradiated nuclear fuels. As part of this effort, work was conducted in FY13 to determine a set of relevant techniques that could be used to improve the overall fuel characterization capabilities, given the constraints associated with highly radioactive materials. An assessment of relevant techniques and facilities available to DOE to perform the characterization was performed. It was determined that a set of x-ray, neutron and proton measurement techniques be further evaluated based on their ability to work with the highly radioactive samples. There were a number of facilities with the techniques mentioned above, that could handle small quantities of high radioactivity samples, but only a few that could handle rodlets or entire fuel rods. Two of those were Idaho National Laboratory (INL) and Los Alamos National Laboratory (LANL). As such, an assessment of the capabilities of each institution was performed, noting the strengths and weaknesses of each. Based on this assessment, a plan was developed in collaboration with INL to establish the process for evaluating both fresh and irradiated fuels, covering shipping, handling, testing and storage of fuel rodlets and materials.

During the early part of FY14, a set of clad depleted uranium dioxide ( $\text{dUO}_2$ ) rodlets with engineered defects and chemistries were measured using neutron radiography (n-RAD), neutron resonance tomography and neutron scattering at LANL to assess the current set of capabilities with respect to spatial resolution and detection limits. A similar evaluation funded by LANL was previously performed in FY10 using proton and neutron radiography on clad  $\text{dUO}_2$  pellets providing initial spatial resolutions and detection limits for the two techniques. Results from the current set of FY14 measurements are summarized below noting several technique improvements and refinements.

Two sets of clad  $\text{dUO}_2$  rodlets sized to mimic light-water reactor (LWR) and fast reactor (FR) rodlets were evaluated using the neutron techniques. The rodlets contained pellets with various defects such as cracks and voids, variations in chemistry, different densities, tungsten wire inclusions for spatial resolution calibration, missing surfaces and additional rodlets containing compressed xenon gas at different pressures. The rodlets were measured with neutron resonance imaging, neutron scattering, and neutron tomography. The spatial resolutions and lower detection limits were established during this process. Refinements and interpretation of the extremely large datasets generated by the measurements were conducted to reconstruct the 3-dimensional (3-D) locations of chemistry, microstructure and phase content. Utilizing the SAMMY code developed at ORNL, a detailed analysis of the transmission spectra was also performed. Since the nuclear cross-sections are known, the code allows the refinement of the area density of the isotope present in the beam path, which in turn allows the derivation of the concentration of the isotopes present

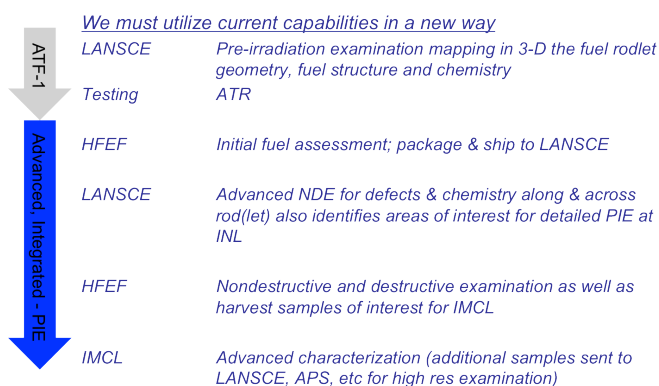
in a given sample. The initial results with known sample thicknesses yielded values within 20% of the expected density values. Also note that the analysis depends on parameters such as background and detector efficiency. Characterization and optimization of these values is currently ongoing.

In terms of A-PIE capability refinement, it was demonstrated that by combining the results from neutron imaging, which uniquely allows the measurement of the concentration of isotopes, with neutron diffraction, crystallography (phases present, strains, crystal structure) and microstructure (defect concentrations, preferred orientation or texture of crystals) can also be obtained. This is shown in figure 23, where a rodlet was fully tomographed and reconstructed to show the distribution of tungsten (artifact due to pellet processing) within the rodlet. By combining these techniques, a determination of the variation in densities and locations of impurities (such as the tungsten) within the rodlet can be attained. The technique can also be used to help to determine the crystallographic form of the tungsten, i.e. metallic tungsten, or a compound with tungsten in it. Additionally, by examining the resonances, gases such as xenon can be detected.



**Figure 23: Neutron imaging and diffraction on  $\text{dUO}_2$  rodlet containing microstructure and void pellets**

In summary, these techniques set the foundation for a strong set of capabilities that have the ability to non-destructively examine fresh and irradiated fuel rodlets for 3-D chemistry, microstructure and phase content with spatial resolutions of 50  $\mu\text{m}$  or less with interpolation and improved analytical routines. These techniques can be tailored to meet fuel development and modeling and simulation needs. Going forward, several additional improvements and refinements will be performed to prepare for evaluation of fresh and irradiated fuel rodlets; including further optimization of the



**Figure 24: Depiction of A-PIE process applied to irradiated fuel rodlets that are shipped to LANL for NDE and back to INL for NDE and destructive examination.**

experimental setup, data analysis and a reduction of background noise. Additionally, a new time-of-flight x-y neutron detector will be put into service to limit possible downtime.



Based on this assessment and the one done for INL, the path forward to testing fresh and irradiated fuels was developed. An idealized depiction of the process is shown in figure 24.

This will rely heavily on coordination of shipping, irradiations and testing to provide data for modeling and simulation and to guide further PIE on fuel rodlets. The key concerns with this plan are the need for a certified shipping cask for irradiated fuels that meet the “Type B” criteria under the US Department of Transportation (DOT) rules and regulations and the coordination of beamtime with shipping schedule.

## 5. Fabrication of Enriched Ceramic Fuels

### 5.1 ATF-1 UN-U<sub>3</sub>Si<sub>5</sub> Composite Fuel Development and Irradiation Test Design

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One approach to development of fuels with enhanced accident tolerance is exploration of advanced composite systems (revolutionary path) with the potential to improve the accident performance of light water reactor fuels as well as offer benefits to normal operation. Composite fuels have been of interest for many decades, as a wide range of both ceramic and metallic alloys can be envisioned that would surpass the performance of traditional LWR oxide ceramic fuels. However, when systems are explored within the constraint of use in existing commercial LWRs, the practical limit on uranium-235 enrichment creates significant challenges in the introduction of non-fissile second phases. Any inert second phase incorporated in a proposed fuel must be limited to extremely low volume fractions if reactor performance is not sacrificed and enrichment remains fixed. It is difficult for such concepts to achieve improvement in any of the critical metrics (e.g. thermal conductivity, mechanical properties, or thermochemical stability) when limited in such a way.

An option to overcome this constraint is the use of uranium bearing second phases. Although they may not contain the uranium density of uranium dioxide or uranium nitride, a phase containing even half the uranium density of these reference ceramics may provide sufficient margin to retain reactor operation within a fixed enrichment. A wide range of uranium

**Table 4: Matrix of uranium-base composite fuel constituents and status with regard to viability screening.**

Matrix/2 <sup>nd</sup> Phase (U g/cm <sup>3</sup> )	UO <sub>2</sub> (9.7)	U <sub>3</sub> O <sub>8</sub> (7.1)	UN (13.5)	U <sub>3</sub> Si <sub>2</sub> (11.3)	U <sub>3</sub> Si <sub>5</sub> (7.5)	UB <sub>2</sub> (11.7)	UB <sub>4</sub> (7.9)
UO <sub>2</sub> (9.7)	Reference Case	Neutronic	Rxn	Rxn	Rxn	Thermo	Thermo
UN (13.5)	Rxn	Rxn	Rxn	WEC FOA	Thermo Neutronic	Thermo	Thermo
U <sub>3</sub> Si <sub>2</sub> (11.3)	Rxn	Rxn	WEC FOA	WEC FOA	Rxn	Rxn (Thermo)	Rxn (Thermo)
UB <sub>2</sub> (11.7)	Thermo				Rxn (Thermo)		
	Discarded due to reaction with 2 <sup>nd</sup> phase or coolant, and/or neutronics						
	Under initial screening						
	Viable after initial screening; continuing for further assessment						

compounds have been investigated historically, many of which could be envisioned to offer intriguing benefits to accident performance as well as the overall fuel attributes. Certain combinations of these phases have the potential to yield the benefits of composite fuels such as improved thermal conductivity and increased pellet integrity while maintaining the current commercial fuel enrichment limit (Table 4). Just as importantly as improvements in accident and normal operation from the fuel pellet itself, fuels with uranium densities higher than  $\text{UO}_2$  can help enable changes to ATF cladding by offsetting the neutronic penalty of candidate systems such as Fe-based cladding, e.g. FeCrAl alloys.

Initial screening of composite fuel concepts has been performed by coordination of thermodynamic, neutronic and assembly level analysis coupled with experimental studies of the fresh fuel properties and characteristics. Based upon the screening results to date, the uranium nitride-uranium silicide composite systems seem attractive and warrant further examination in terms of fresh fuel properties and more detailed reactor performance analysis (see for example the highlights on property studies on uranium silicide phases by J.T. White and composite fuel reactor performance and safety analysis by N. Brown). There currently exists limited data for fresh fuel properties of a number of the constituent phases of the candidate composite systems and the composites themselves but there is even less data in terms of irradiation behavior. Therefore, an initial irradiation test has been initiated under the ATF-1 irradiation test series for the UN- $\text{U}_3\text{Si}_5$  composite fuel system. As can be seen from Table 5, of the nitride-silicide systems that have been considered, UN- $\text{U}_3\text{Si}_2$  is being explored under the Westinghouse FOA. The UN- $\text{U}_3\text{Si}_5$  is also a promising system based upon early assessment as the  $\text{U}_3\text{Si}_5$  phase has a fairly high thermal conductivity (Fig. 12), and relative to  $\text{U}_3\text{Si}_2$ , has better oxidation behavior in steam (Fig. 13) and a higher melting point (Fig. 6). However, the irradiation stability of the UN- $\text{U}_3\text{Si}_5$  composite and of the  $\text{U}_3\text{Si}_5$  phase are unknown and must be assessed to further evaluate the viability of this system.

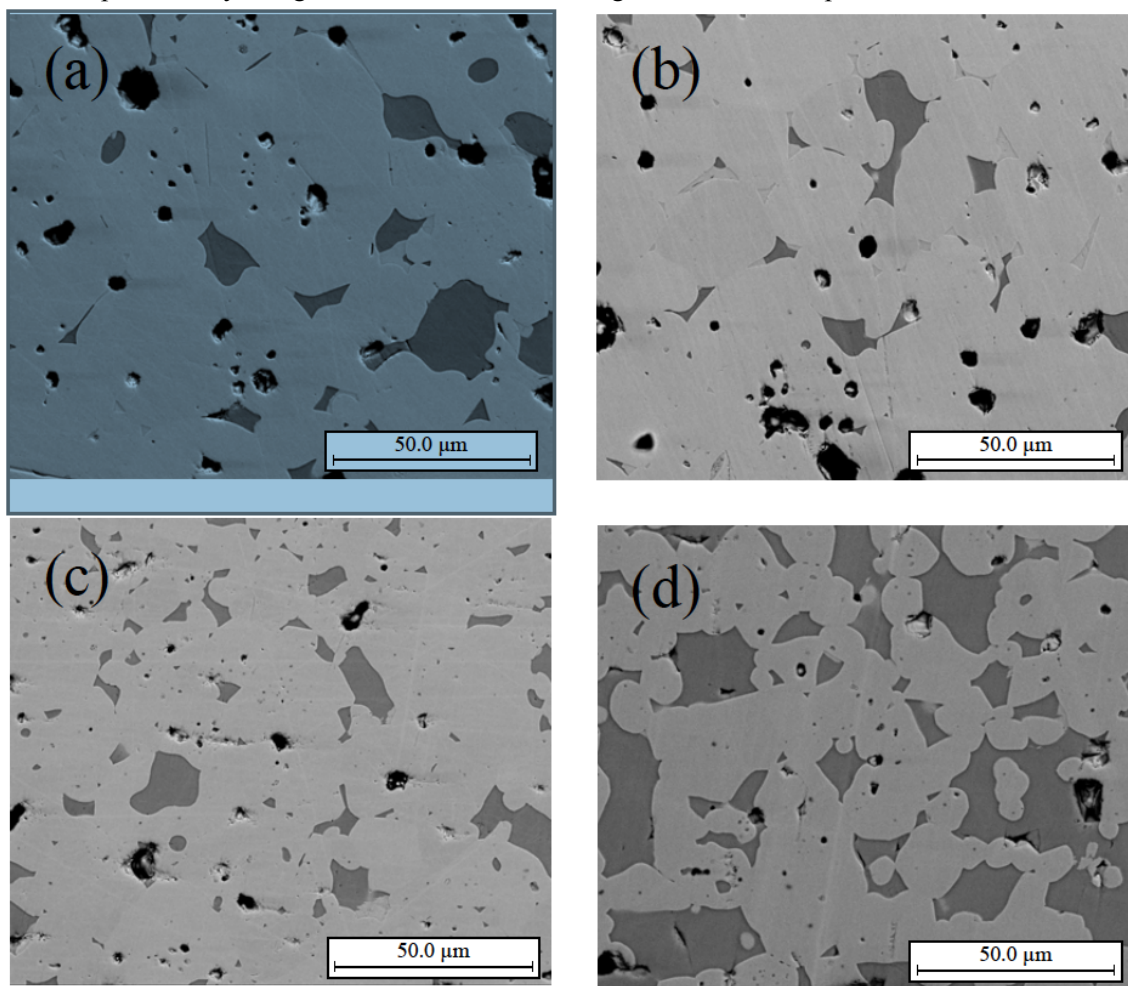
Therefore, preliminary design in fuel fabrication process development for an initial drop-in type irradiation test has been undertaken in FY14. The test will be performed in the Advanced Test Reactor (ATR) as part of the ATF-1 test series with the designation of “LANL-1” and will consist of two rodlets of UN- $\text{U}_3\text{Si}_5$  composite fuel and two rodlets of  $\text{U}_3\text{Si}_5$  monolithic fuel. The nominal test parameters are shown in Table 5 where highest priority was place on linear heat

**Table 5: ATF-1/LANL-1 nominal test design parameters.**

Fuel	PICT Target/Max (°C)	LHGR (W/cm)	Centerline Temp (°C)	Cladding Material	Target Burnup (GWd/MTU)
UN/15vol% $\text{U}_3\text{Si}_5$	350/400	240	<1650	Kanthal AF	10
UN/15vol% $\text{U}_3\text{Si}_5$	350/400	240	<1650	Kanthal AF	20
UN/15vol% $\text{U}_3\text{Si}_5$	350/400	240	<1650	Kanthal AF	50
$\text{U}_3\text{Si}_5$	350/400	240	<1650	Kanthal AF	10
$\text{U}_3\text{Si}_5$	350/400	240	<1650	Kanthal AF	20

generation rate (LHGR) and then on peak internal cladding temperature (PICT). While monolithic  $\text{U}_3\text{Si}_5$  is not being advocated as a stand alone fuel concept – due to the relatively low uranium density of  $7.5 \text{ g/cm}^3$  a  $\text{U}_3\text{Si}_5$  fuel would require enrichment great than 5%  $^{235}\text{U}$  – the silicide-only rodlets are being irradiated as an efficient way to collect irradiation behavior data for this composite constituent phase.

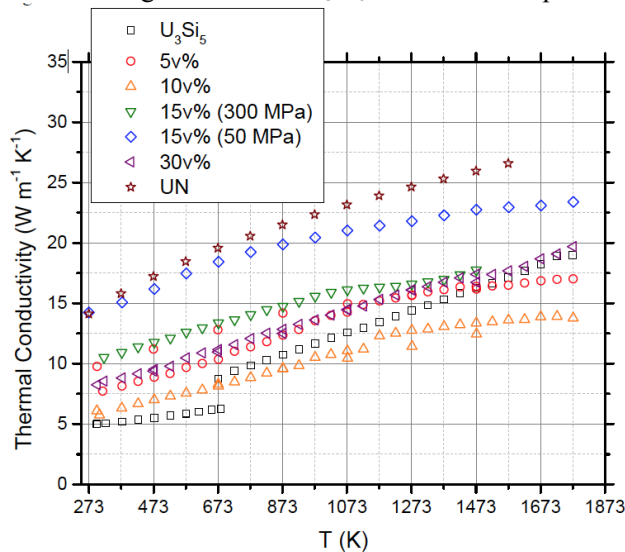
The preliminary design of the test required material properties that are not available from literature so processes were developed to fabricate material property samples with densities of greater than 90% theoretical density (typically >95%) for the UN and  $\text{U}_3\text{Si}_5$  constituent phases as well as the UN- $\text{U}_3\text{Si}_5$  composite. Representative microstructures of the composite samples (Fig. 25) show that the silicide phase does not coat the UN grain boundaries and is a discontinuous phase. Key properties such as thermal conductivity (Fig. 26) were measured and subsequently used for preliminary design of the LANL-1 test using the BISON fuel performance code.



**Figure 25: Microstructures of  $\text{U}_3\text{Si}_5$ -UN collected using a backscatter detector for (a) 5v%, (b) 10v%, (c) 15v%, and (d) 30 v% specimens.**

The preliminary LANL-1 fuel and rodlet design was performed using the BISON code modified to initially utilize composite fuel properties based on a rule-of-mixtures approximation from the measured constituent properties. Subsequently the analysis was performed using the properties measured on the actual UN-15vol%  $\text{U}_3\text{Si}_5$  composite samples matching the target fuel density of 95% theoretical density (Fig. 26). The composite data was in fairly good agreement

with the rule-of-mixtures initial approximation. The preliminary composite test geometry from the BISON analysis is shown in Figure 27 and of key test temperatures are shown in Figure 28. The LANL-1 test is designed with a rather large rodlet/capsule gap of  $\sim 70\mu\text{m}$  to facilitate neutron tomography to image the gap before and after irradiation (detector pixel pitch of  $55\mu\text{m}$ ). As there is no swelling data for the  $\text{U}_3\text{Si}_5$  or for the composite at this time, indeed this data is one of the



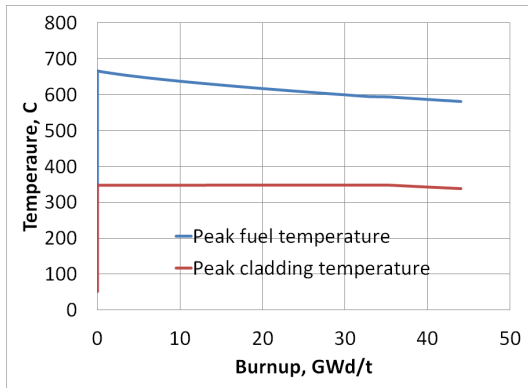
**Figure 26: Thermal conductivity values for UN- $\text{U}_3\text{Si}_5$  composite specimens calculated as a function of temperature from measured thermal diffusivity, thermal expansion and specific heat values. Note: the 15vol% 300MPa data is artificially low and is included to illustrate conductivity degradation due to internal cracking. The 50MPa data is the values use**

primary objectives of the LANL-1 test, swelling was estimated using a model for UN from fast reactor testing. Using this approximation, the pellet/capsule gap was set at  $25\mu\text{m}$  where closure is not predicted until  $\sim 35\text{ GWd/t}$  burnup (Fig. 29).

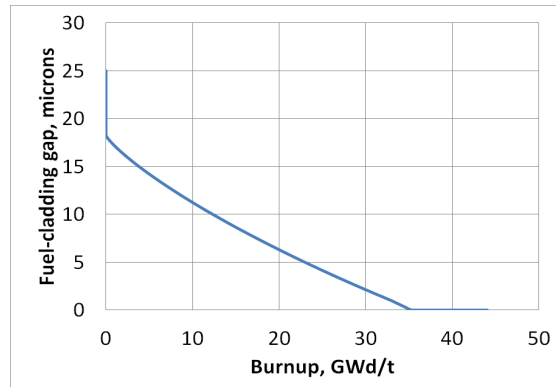
The preliminary design using BISON has enabled early development of the fuel fabrication process. Final design approval using the ATR-approved tools is anticipated for early in FY15. At that point, final refinement of the fabrication process will be completed and fuel pellets will be fabricate and shipping to INL for fabrication of the test rodlets and encapsulation. Insertion of the ATF-1 LANL-1 test is planned for the ATR 158A run cycle.

Rodlet		Fuel		Capsule	
Design Parameter	Nominal Value	Design Parameter	Nominal Value	Design Parameter	Nominal Value
Cladding Material	Kanthal AF (FeCrAl alloy)	Fuel Type	UN-15v% $\text{U}_3\text{Si}_5$ $\text{U}_3\text{Si}_5$	Capsule Material	316L SS
Cladding O.D.	0.3708 in (9.4194 mm)	Enrichment	<4.95	Capsule O.D.	0.4320 in (10.9728 mm)
Cladding I.D.	0.3306 in (8.3984 mm)	Pellet O.D.	0.3287 in (8.3484 mm)	Capsule I.D.	0.3760 in (9.5504 mm)
Bond Material	He	Pellet Length	$\geq 0.362$ in (9.18 mm)	Capsule Length	6.16 in (156.46 mm)
		Stack Length	3.20 in (45 mm)	Capsule/Rodlet Gap	$\sim 0.0028$ in (0.071 mm)

**Figure 27: Preliminary composite test geometry from the BISON analysis to target a 240W/cm LHGR while maintaining a  $\leq 350^\circ\text{C}$  PICT.**



**Figure 28: Peak fuel and cladding temperatures as a function of burnup for UN-15vol%U<sub>3</sub>Si<sub>5</sub> composite fuel in Kanthal AF cladding from the preliminary BISON**



**Figure 29: Fuel-cladding gap as a function of burnup for UN-15vol%U<sub>3</sub>Si<sub>5</sub> composite fuel in Kanthal AF cladding from the preliminary BISON analysis.**



## 6. FY14 Ceramic Fuels Publications

1. J.W. McMurray, D. Shin, B.W. Slone, T.M. Besmann, "Thermochemical modeling of the  $U_{1-y}Gd_yO_{2+x}$  phase," *J. Nuc. Mater.*, **443**, pp. 588-595(2013)
2. J.T. White, A.T. Nelson, D.D. Byler, J.A. Valdez, K.J. McClellan, "Thermophysical properties of  $U_3Si$ ," *Journal of Nuclear Materials*, **452** (2014) 302.
3. J.T. White, A.T. Nelson, J.T. Dunwoody, D.D. Byler, D.J. Safarik, K.J. McClellan, "Thermophysical properties of  $U_3Si_5$  to 1773 K," *accepted in the Journal of Nuclear Materials* (2014).
4. A.T. Nelson, D.R. Rittman, J.T. White, J.T. Dunwoody, M. Kato and K.J. McClellan, "An Evaluation of the Thermophysical Properties of Stoichiometric  $CeO_2$  in Comparison to  $UO_2$  and  $PuO_2$ ," *J. Am. Ceram. Soc.*, DOI: 10.1111/jace.13170 (online 7 AUG 2014).
5. N.R. Brown, A. Aronson, M. Todosow, R. Brito, K.J. McClellan, "Neutronic performance of uranium nitride composite fuels in a PWR," *Nuc. Eng. and Design*, **275**, pp. 393-407 (2014)
6. J.T. White, A.T. Nelson, D.D. Byler, J.A. Valdez, and K.J. McClellan, "Thermophysical Properties of  $U_3Si$  to 1150K," *J. Nuc. Mater.*, **452**, pp. 304-310 (2014)
7. I.O. Usov, R.M. Dickerson, P.O. Dickerson, D.D. Byler, and K.J. McClellan, "Uranium dioxide films with xenon filled bubbles for fission gas behavior studies," *J. Nuc. Mater.*, **452**, pp. 173-177 (2014)
8. J.W.L. Pang, A. Chernatynskiy, B.C. Larson, W.J.L. Buyers, D.L. Abernathy, K.J. McClellan, and S.R. Phillpot, "Phonon Density of States and Anharmonicity of  $UO_2$ ," *Phys. Rev. B*, **89** pp. 115132-11 (2014)
9. A.T. Nelson, J.T. White, D.A. Andersson, J.A. Aguiar, K.J. McClellan, D.D. Byler, M.P. Short and C.R. Stanek, "Thermal Expansion, Heat Capacity, and Thermal Conductivity of Nickel Ferrite ( $NiFe_2O_4$ ).," *J. Am. Ceram. Soc.*, **97**[5], pp.1559-1565 (2014)
10. M. Kato, T. Murakami, T. Sunaoshi, A. T. Nelson, and K. J. McClellan, "Property measurements of  $(U_{0.7}Pu_{0.3})O_{2-x}$  in  $PO_2$ -controlled atmosphere," Proceedings Global 2013, Salt Lake City, Utah, Sept. 29- Oct. 2, 2013.
11. N. R. Brown, M. Todosow, K. J. McClellan, "Uranium nitride composite fuels in a pressurized water reactor: exploration of multi-batch cycle length and UB4 admixture for reactivity control", Proceedings of *PHYSOR 2014 – The Role of Reactor Physics Toward a Sustainable Future*, Kyoto, Japan September 28 – October 3 (2014).
12. J.W. McMurray, D. Shin, B.W. Slone, T.M. Besmann, "Thermodynamic reassessment of U-Gd-O system," *J. Nuc. Mater.*, **452**, pp. 397-406(2014)